

Sauget Area 2 Sites Group

April 14th, 2008

Mr. Ross del Rosario
U. S. Environmental Protection Agency, Region 5
77W. Jackson Blvd. (SR-6J)
Chicago, IL 60604-3590

Re: Sauget Area-wide Groundwater Model

OVERNIGHT MAIL

Dear Ross:

Attached, is the previously approved Regional Groundwater Flow and Contaminant Transport Model for the American Bottoms Aquifer incorporating the changes proposed in the GSI, November 20, 2007 response to comments.

Any questions, please advise.

Sincerely,

Gary Uphoff.
By, S.D. Smith

Gary D. Uphoff
Co-Project Coordinator



Steven D. Smith
Co-Project Coordinator

cc: Distribution List Attached

DISTRIBUTION LIST

Ross del Rosario – 1 Hard Copy with CD
U.S. Environmental Protection Agency
Superfund Division
77 West Jackson Blvd. (SR-6J)
Chicago, IL 60604
312-886-6840

Sandra Bron – 2 Hard Copies with 2 CDs
Illinois EPA
Bureau of Land, FSRS/NPL Unit
1021 North Grand Avenue East
P.O. box 19276
Springfield, Illinois 62794-9276

Lisa Cundiff – 1 Hard Copies with 1 CD
CH2M HILL
727 North First Street
Suite 400
St. Louis, MO 63102
314-421-0313

Steve Smith – 1 Hard Copies with CD
Solutia
575 Maryville Centre Drive, 2 N
St. Louis, MO 63141

Sauget Area 2 Sites Group – CD

Regional Groundwater Flow and Contaminant Transport Model

American Bottoms Aquifer



Submitted to:
Mr. Steve Shroff, URS Corp.

April 14, 2008

GSI Environmental Inc.
2211 Norfolk, Suite 1000, Houston, TX 77098

TABLE OF CONTENTS

EXECUTIVE SUMMARY	ES-1
-------------------------	------

PART 1: Development of Flow Model

FLOW MODEL EXECUTIVE SUMMARY	FLOW-1
1.0 INTRODUCTION.....	FLOW-3
2.0 AREA DESCRIPTION	FLOW-3
3.0 HYDROGEOLOGIC CHARACTERIZATION.....	FLOW-3
4.0 PREVIOUS MODELS	FLOW-3
5.0 MODEL OBJECTIVES	FLOW-4
6.0 MODEL DESCRIPTION	FLOW-4
6.1 Model Grid.....	FLOW-5
6.2 Model Capabilities.....	FLOW-5
6.3 Model Domain Boundary Conditions.....	FLOW-5
6.4 Model Layers.....	FLOW-5
6.5 Mississippi River	FLOW-6
6.6 Hydraulic Conductivity.....	FLOW-6
6.7 Surface Infiltration	FLOW-7
6.8 Highway Dewatering Projects	FLOW-7
6.9 GMCS System	FLOW-7
6.10 Porosity	FLOW-8
6.11 Transient Flow – Storage Coefficients	FLOW-8
6.12 Head Observation Wells	FLOW-8
7.0 MODEL CALIBRATION	FLOW-8
7.1 1962 Semi-Qualitative Comparison	FLOW-9
7.2 1990 Semi-Qualitative Comparison	FLOW-9
7.3 2002 Qualitative Comparison	FLOW-10
7.4 2005 Quantitative Comparison.....	FLOW-10
7.5 Final Calibration Results	FLOW-14
8.0 SENSITIVITY ANALYSIS.....	FLOW-16
9.0 MODEL LIMITATIONS.....	FLOW-17
10.0 FINAL MODEL PARAMETERS	FLOW-18
11.0 REFERENCES.....	FLOW-21

PART 1: Tables

Table 1	Boring Log Data Used in Groundwater Flow Model
Table 2	River Bottom Profile Elevations Used in Model
Table 3	Mississippi River Sediment Bed Conductivity Used in Model
Table 4	Groundwater Flow Model Calibration Residuals
Table 5	Groundwater Flow Model Calibration Statistics

PART 1: Figures

Figure 1	Model Domain
Figure 2	Generalized Hydrogeologic Cross-Section
Figure 3	Model Grid – Overall
Figure 4	Model Grid – Site Only
Figure 5	Model Boundary Conditions
Figure 6	Ground Surface Elevations – Overall
Figure 7	Ground Surface Elevations – Site Only
Figure 8	Top of Middle Hydrogeologic Unit Elevations – Overall
Figure 9	Top of Middle Hydrogeologic Unit Elevations – Site Only
Figure 10	Top of Deep Hydrogeologic Unit Elevations – Overall
Figure 11	Top of Deep Hydrogeologic Unit Elevations – Site Only
Figure 12	Bedrock Elevations – Overall
Figure 13	Bedrock Elevations – Site Only
Figure 14	Thickness of the Shallow Hydrogeologic Unit – Overall
Figure 15	Thickness of the Shallow Hydrogeologic Unit – Site Only
Figure 16	Thickness of the Middle Hydrogeologic Unit – Overall
Figure 17	Thickness of the Middle Hydrogeologic Unit – Site Only
Figure 18	Thickness of the Deep Hydrogeologic Unit – Overall
Figure 19	Thickness of the Deep Hydrogeologic Unit – Site Only
Figure 20	West-East Cross-Section Across EW-2
Figure 21	Modeled Mississippi River
Figure 22	Cross-section Locations Across Modeled Mississippi River
Figure 23	US Army Corps of Engineer Bathymetry Data
Figure 24	Model Hydraulic Conductivity Arrays
Figure 25	Model Surface Infiltration
Figure 26	Locations of Water Level Observation Wells
Figure 27	Model Output: 1962 Potentiometric Surface Map
Figure 28	Measured 1962 Potentiometric Surface Map
Figure 29	Model Output: 1990 Potentiometric Surface Map
Figure 30	Measured 1990 Potentiometric Surface Map
Figure 31	Model Output: 2002 Potentiometric Surface Map
Figure 32	Measured 2002 Potentiometric Surface Map
Figure 33	Simulated Industrial and Dewatering Wells Used in Model
Figure 34	Model Output: 2005 Potentiometric Surface Map – SHU Overall
Figure 35	Model Output: 2005 Potentiometric Surface Map – SHU Site Only
Figure 36	Measured 2005 Potentiometric Surface Map – SHU
Figure 37	Model Output: 2005 Potentiometric Surface Map – MHU Overall
Figure 38	Model Output: 2005 Potentiometric Surface Map – MHU Site Only
Figure 39	Measured 2005 Potentiometric Surface Map – MHU
Figure 40	Model Output: 2005 Potentiometric Surface Map – DHU Overall
Figure 41	Model Output: 2005 Potentiometric Surface Map – DHU Site Only
Figure 42	Measured 2005 Potentiometric Surface Map – DHU
Figure 43	Spatial Correlation Between Simulated and Measured Water Levels – SHU

PART 1: Figures Cont'd

Figure 44	Spatial Correlation Between Simulated and Measured Water Levels – MHU
Figure 45	Spatial Correlation Between Simulated and Measured Water Levels – DHU
Figure 46	Scattergram of Simulated Vs Measured Water Levels – SHU
Figure 47	Scattergram of Simulated Vs Measured Water Levels – MHU
Figure 48	Scattergram of Simulated Vs Measured Water Levels – DHU
Figure 49	Scattergram of Simulated Vs Measured Water Levels – Overall

PART 2: Development of Contaminant Transport Model

CONTAMINANT TRANSPORT MODEL EXECUTIVE SUMMARY	TRANSPORT-1
1.0 INTRODUCTION.....	TRANSPORT-5
2.0 AREA DESCRIPTION.....	TRANSPORT-5
3.0 MODEL OBJECTIVES	TRANSPORT-5
4.0 CONTAMINANT TRANSPORT MODEL DESCRIPTION	TRANSPORT-6
4.1 Model Capabilities	TRANSPORT-6
4.2 Decay Model	TRANSPORT-6
4.3 Porosity	TRANSPORT-6
4.4 Constituents of Concern (COC).....	TRANSPORT-6
4.5 Source Assignment	TRANSPORT-6
4.6 Source Concentrations.....	TRANSPORT-7
4.7 Initial Concentrations.....	TRANSPORT-8
4.8 Biodegradation and Sorption.....	TRANSPORT-8
4.9 Source Decay.....	TRANSPORT-9
4.10 Dispersion	TRANSPORT-9
4.11 Concentration Observation Wells.....	TRANSPORT-10
4.12 Hydraulic Conductivity	TRANSPORT-10
5.0 MODEL CALIBRATION	TRANSPORT-10
5.1 Initial Qualitative Model Comparison.....	TRANSPORT-11
5.2 Quantitative Calibration	TRANSPORT-12
5.3 Base Case Model – Calibration Results.....	TRANSPORT-12
5.3.1 Biodegradation Rate Constant Study.....	TRANSPORT-13
5.3.2 Source Decay Life Time Study.....	TRANSPORT-16
5.3.3 Reactive Transport Study (RT3D vs. MT3D)	TRANSPORT-16
5.3.4 Vertical Gradient Study (Flow model)	TRANSPORT-17
5.3.5 North Plant Pumping Study.....	TRANSPORT-18
5.3.6 Transient Recharge and Mississippi River Stage Study.....	TRANSPORT-18
5.3.7 Historical Industrial Wells Study.....	TRANSPORT-18
5.4 Final Calibration	TRANSPORT-19
Highway Dewatering Well Pumping Rates	TRANSPORT-19
Infiltration Rate.....	TRANSPORT-19
Porosity.....	TRANSPORT-19
Chemical Specific Parameters.....	TRANSPORT-20
Biodegradation Rate Constant.....	TRANSPORT-20

Source Area.....	TRANSPORT-21
Source Concentration	TRANSPORT-21
5.5 Mass Flux	TRANSPORT-21
6.0 FINAL MODEL CALIBRATION RESULTS.....	TRANSPORT-22
6.1 Quality of Fit Between Actual and Predicted Concentrations	TRANSPORT-22
6.2 Predicted Plume Extent in 2038	TRANSPORT-25
6.3 Capture of 2038 Plumes by the GMCS	TRANSPORT-25
6.4 Capture of Source Area Plumes by the GMCS	TRANSPORT-26
All Source Areas	TRANSPORT-27
Sauget Area 1 Source Areas Only.....	TRANSPORT-28
Sauget Area 2 Source Areas Only – Combined	TRANSPORT-29
Sauget Area 2 Source Areas – Site R Only	TRANSPORT-30
Sauget Area 2 Source Areas – Site O Only.....	TRANSPORT-31
Clayton Chemical Source Areas Only	TRANSPORT-32
W.G. Krummrich Source Areas Only.....	TRANSPORT-33
Mass Flux Discussion	TRANSPORT-34
7.0 SENSITIVITY ANALYSIS.....	TRANSPORT-35
8.0 MODEL LIMITATIONS	TRANSPORT-37
9.0 REFERENCES.....	TRANSPORT-38

PART 2: Appendices

- Appendix 1 Sauget Area 2 Focused Feasibility Study
- Appendix 2 Source Evaluation Study
- Appendix 3 Time to Clean Estimates
- Appendix 4 Groundwater Chloride Concentrations
- Appendix 5 Source Area Wells and Observed Concentrations
- Appendix 6 Mass Flux Results

PART 2: Tables

Table 1	Groundwater Pumping Rates Used in Calibrated Model
Table 2	Chlorobenzene Site R Calibration Results
Table 3a	Groundwater Fate and Transport Model Calibration Results – Chlorobenzene
Table 3b	Groundwater Fate and Transport Model Calibration Results – 1,4-Dichlorobenzene
Table 3c	Groundwater Fate and Transport Model Calibration Results – 2,4- Dichlorophenoxyacetic Acid
Table 3d	Groundwater Fate and Transport Model Calibration Results – Tetrachloroethene
Table 3e	Groundwater Fate and Transport Model Calibration Results – Trichloroethene
Table 3f	Groundwater Fate and Transport Model Calibration Results – cis-1,2-Dichloroethene

Table 3g Groundwater Fate and Transport Model Calibration Results –
Vinyl Chloride

PART 2: Figures

Figure 1	Model Domain
Figure 2	Qualitative Calibration Case 1 – MHU
Figure 3	Qualitative Calibration Case 1 – DHU
Figure 4	Qualitative Calibration Case 2 – MHU
Figure 5	Qualitative Calibration Case 2 – DHU
Figure 6	Qualitative Calibration Case 3 – MHU
Figure 7	Qualitative Calibration Case 3 – DHU
Figure 8	Qualitative Calibration Case 4 – MHU
Figure 9	Qualitative Calibration Case 4 – DHU
Figure 10	Qualitative Calibration Case 5 – MHU
Figure 11	Qualitative Calibration Case 5 – DHU
Figure 12	Qualitative Calibration Case 6 – MHU
Figure 13	Qualitative Calibration Case 6 – MHU
Figure 14	Simulated Industrial and Dewatering Wells Used in Model
Figure 15	Qualitative Calibration Case 7 – MHU
Figure 16	Qualitative Calibration Case 7 – DHU
Figure 17	Chlorobenzene Source Areas and Concentrations – SHU
Figure 18	Chlorobenzene Source Areas and Concentrations – MHU
Figure 19	Chlorobenzene Source Areas and Concentrations – DHU
Figure 20	1,4-Dichlorobenzene Source Areas and Concentrations – SHU
Figure 21	1,4-Dichlorobenzene Source Areas and Concentrations – MHU
Figure 22	1,4-Dichlorobenzene Source Areas and Concentrations – DHU
Figure 23	2,4-Dichlorophenoxyacetic acid Source Areas and Concentrations – SHU
Figure 24	2,4-Dichlorophenoxyacetic acid Source Areas and Concentrations – MHU
Figure 25	Chlorinated Solvents Source Areas and Concentrations – SHU
Figure 26	Chlorinated Solvents Source Areas and Concentrations – MHU
Figure 27	Chlorinated Solvents Source Areas and Concentrations – DHU
Figure 28	Mass Flux Zone Budget Zones – SHU
Figure 29	Mass Flux Zone Budget Zones – MHU
Figure 30	Mass Flux Zone Budget Zones – DHU
Figure 31	Calibrated Chlorobenzene Plume – 2006 – SHU
Figure 32	Calibrated Chlorobenzene Plume – 2006 – MHU
Figure 33	Calibrated Chlorobenzene Plume – 2006 – DHU
Figure 34	Simulated Chlorobenzene Plume – 2006 and 2038 – SHU
Figure 35	Simulated Chlorobenzene Plume – 1980 and 2000 – MHU
Figure 36	Simulated Chlorobenzene Plume – 2006 and 2038 – MHU
Figure 37	Simulated Chlorobenzene Plume – 1980 and 2000 – DHU
Figure 38	Simulated Chlorobenzene Plume – 2006 and 2038 – DHU
Figure 39	Spatial Correlation Between Simulated and Measured Concentration Levels – Chlorobenzene – SHU

PART 2: Figures Cont'd

Figure 40	Spatial Correlation Between Simulated and Measured Concentration Levels – Chlorobenzene – MHU
Figure 41	Spatial Correlation Between Simulated and Measured Concentration Levels – Chlorobenzene – DHU
Figure 42	Calibrated 1,4-Dichlorobenzene Plume – 2006 – SHU
Figure 43	Calibrated 1,4-Dichlorobenzene Plume – 2006 – MHU
Figure 44	Calibrated 1,4-Dichlorobenzene Plume – 2006 – DHU
Figure 45	Simulated 1,4-Dichlorobenzene Plume – 2006 and 2038 – SHU
Figure 46	Simulated 1,4-Dichlorobenzene Plume – 1980 and 2000 – MHU
Figure 47	Simulated 1,4-Dichlorobenzene Plume – 2006 and 2038 – MHU
Figure 48	Simulated 1,4-Dichlorobenzene Plume – 1980 and 2000 – DHU
Figure 49	Simulated 1,4-Dichlorobenzene Plume – 2006 and 2038 – DHU
Figure 50	Spatial Correlation Between Simulated and Measured Concentration Levels – 1,4-Dichlorobenzene – SHU
Figure 51	Spatial Correlation Between Simulated and Measured Concentration Levels – 1,4-Dichlorobenzene – MHU
Figure 52	Spatial Correlation Between Simulated and Measured Concentration Levels – 1,4-Dichlorobenzene – DHU
Figure 53	Calibrated 2,4-Dichlorophenoxyacetic acid Plume – 2006 – SHU
Figure 54	Calibrated 2,4-Dichlorophenoxyacetic acid Plume – 2006 – MHU
Figure 55	Calibrated 2,4-Dichlorophenoxyacetic acid Plume – 2006 – DHU
Figure 56	Simulated 2,4-Dichlorophenoxyacetic acid Plume – 2006 and 2038 – SHU
Figure 57	Simulated 2,4-Dichlorophenoxyacetic acid Plume – 1980 and 2000 – MHU
Figure 58	Simulated 2,4-Dichlorophenoxyacetic acid Plume – 2006 and 2038 – MHU
Figure 59	Simulated 2,4-Dichlorophenoxyacetic acid Plume – 1980 and 2000 – DHU
Figure 60	Simulated 2,4-Dichlorophenoxyacetic acid Plume – 2006 and 2038 – DHU
Figure 61	Spatial Correlation Between Simulated and Measured Concentration Levels – 2,4-Dichlorophenoxyacetic acid – SHU
Figure 62	Spatial Correlation Between Simulated and Measured Concentration Levels – 2,4-Dichlorophenoxyacetic acid – MHU
Figure 63	Spatial Correlation Between Simulated and Measured Concentration Levels – 2,4-Dichlorophenoxyacetic acid – DHU
Figure 64	Calibrated PCE Plume – 2006 – SHU
Figure 65	Calibrated PCE Plume – 2006 – MHU
Figure 66	Calibrated PCE Plume – 2006 – DHU
Figure 67	Simulated PCE Plume – 2006 and 2038 – SHU
Figure 68	Simulated PCE Plume – 2006 and 2038 – MHU
Figure 69	Simulated PCE Plume – 2006 and 2038 – DHU
Figure 70	Spatial Correlation Between Simulated and Measured Concentration Levels – PCE – SHU

PART 2: Figures Cont'd

Figure 71	Spatial Correlation Between Simulated and Measured Concentration Levels – PCE – MHU
Figure 72	Spatial Correlation Between Simulated and Measured Concentration Levels – PCE – DHU
Figure 73	Calibrated TCE Plume – 2006 – SHU
Figure 74	Calibrated TCE Plume – 2006 – MHU
Figure 75	Calibrated TCE Plume – 2006 – DHU
Figure 76	Simulated TCE Plume – 2006 and 2038 – SHU
Figure 77	Simulated TCE Plume – 2006 and 2038 – MHU
Figure 78	Simulated TCE Plume – 2006 and 2038 – DHU
Figure 79	Spatial Correlation Between Simulated and Measured Concentration Levels – TCE – SHU
Figure 80	Spatial Correlation Between Simulated and Measured Concentration Levels – TCE – MHU
Figure 81	Spatial Correlation Between Simulated and Measured Concentration Levels – TCE – DHU
Figure 82	Calibrated 12-DCE Plume – 2006 – SHU
Figure 83	Calibrated 12-DCE Plume – 2006 – MHU
Figure 84	Calibrated 12-DCE Plume – 2006 – DHU
Figure 85	Simulated 12-DCE Plume – 2006 and 2038 – SHU
Figure 86	Simulated 12-DCE Plume – 1980 and 2000 – MHU
Figure 87	Simulated 12-DCE Plume – 2006 and 2038 – MHU
Figure 88	Simulated 12-DCE Plume – 1980 and 2000 – DHU
Figure 89	Simulated 12-DCE Plume – 2006 and 2038 – DHU
Figure 90	Spatial Correlation Between Simulated and Measured Concentration Levels – 12-DCE – SHU
Figure 91	Spatial Correlation Between Simulated and Measured Concentration Levels – 12-DCE – MHU
Figure 92	Spatial Correlation Between Simulated and Measured Concentration Levels – 12-DCE – DHU
Figure 93	Calibrated Vinyl Chloride Plume – 2006 – SHU
Figure 94	Calibrated Vinyl Chloride Plume – 2006 – MHU
Figure 95	Calibrated Vinyl Chloride Plume – 2006 – DHU
Figure 96	Simulated Vinyl Chloride Plume – 2006 and 2038 – SHU
Figure 97	Simulated Vinyl Chloride Plume – 1980 and 2000 – MHU
Figure 98	Simulated Vinyl Chloride Plume – 2006 and 2038 – MHU
Figure 99	Simulated Vinyl Chloride Plume – 1980 and 2000 – DHU
Figure 100	Simulated Vinyl Chloride Plume – 2006 and 2038 – DHU
Figure 101	Spatial Correlation Between Simulated and Measured Concentration Levels – Vinyl Chloride – SHU
Figure 102	Spatial Correlation Between Simulated and Measured Concentration Levels – Vinyl Chloride – MHU
Figure 103	Spatial Correlation Between Simulated and Measured Concentration Levels – Vinyl Chloride – DHU

DEVELOPMENT OF A REGIONAL GROUNDWATER FLOW AND CONTAMINANT TRANSPORT MODEL

EXECUTIVE SUMMARY

Background and Objectives

The southern portion of the American Bottoms aquifer is or has the potential to be affected by constituents originating from several facilities and waste management sites. Although several previous modeling efforts have focused on the American Bottoms aquifer, there was no single integrated flow and fate and transport model that could evaluate all sites of interest on a regional scale.

GSI Environmental Inc. (GSI), formerly known as Groundwater Services, Inc., was retained by URS Corporation to develop a regional groundwater flow and contaminant transport model covering the southern portion of the American Bottoms aquifer. This area includes the Sauget Area 1 (SA1) sites, the Sauget Area 2 (SA2) sites, and the Krummrich facility (Krummrich) in and around the Village of Sauget and the Village of Cahokia in St. Clair County, Illinois. Other sites of interest include ConocoPhillips East St. Louis Terminal and Clayton Chemical facility.

The objectives of this modeling project, as stated in the Groundwater Modeling Plan (GSI, 2006), were to upgrade/enhance the GSI 2001-2005 groundwater model into a regional model encompassing the Sauget/Cahokia areas such that

- 1) the modeled flow paths can be validated using actual plume measurements made during the RI phase;
- 2) a sensitivity analysis can be performed to assess how groundwater flow and contaminant nature and extent respond under various remedial alternatives during the FS phase;
- 3) the capture zone of the Sauget Area 2 GMCS can be further defined; and
- 4) the vertical mass flux of chemicals can be evaluated from both a site-specific and a regional perspective.

In addition, the model can be calibrated to explain constituents at locations identified as locations of concern by the U.S. Environmental Protection Agency (EPA).

This report describes the development and calibration of the flow and contaminant transport model. The report is divided into two sections:

- a) Part 1: describes the development and calibration of the flow portion of the model, while
- b) Part 2: describes the development and calibration of the contaminant transport portion of the model.

RESULTS

Groundwater Flow Model

The MODFLOW groundwater flow model was developed using data from previous hydrogeologic characterization projects, existing groundwater models, and new data developed as part of the SA1, SA2, and Krummrich site investigations. The groundwater model was then calibrated so that the simulated water levels in the model were representative of several actual potentiometric (water level) maps of data collected in 1962, 1990, and 2005. During calibration, model inputs such as river conductance, boundary conditions, pumping rates from wells, Mississippi River stage, and hydraulic conductivity were adjusted to reduce the difference between measured and simulated groundwater levels.

During the development of the contaminant transport model, changes were made to the groundwater flow model (GSI, 2006b) in an attempt to meet the goals stated earlier.

The final model simulates the regional aquifer system with an overall root mean squared (RMS) error of 0.7 ft and mean residual (MR) error of 0.06 ft for the model calibration to July 2005 water level data. Individual RMS errors of 0.8 ft, 0.6 ft, and 0.6 ft were obtained for the Shallow Hydrogeologic Unit (SHU), Middle Hydrogeologic Unit (MHU), and Deep Hydrogeologic Unit (DHU), respectively. Individual MR errors of 0.1 ft, 0.01 ft, and -0.06 ft were obtained for the SHU, MHU, and DHU, respectively. These RMS error values indicate that, in general, simulated water levels closely match actual water levels.

Contaminant Transport Model

The American Bottoms Regional Groundwater Contaminant Transport model was developed using data from previous hydrogeologic characterization projects, existing groundwater models, and data developed as part of the SA1 sites, SA2 sites, and Krummrich facility investigations. The MODFLOW groundwater model was then calibrated so that groundwater concentrations simulated in the model were representative of measured groundwater concentrations observed in 2005 and 2006. During calibration, model inputs such as source concentrations, biodegradation rates, dispersion, recharge, pumping rates from certain identified wells, and horizontal hydraulic conductivity were adjusted to reduce the difference between simulated and observed concentration levels. The calibration resulted in a conservative model that may overpredict the impacts of some site constituents.

Two fate and transport models (RT3D for chlorinated solvents and MT3D for all other constituents) were used to simulate the movement of groundwater plumes from the source zones in the model domain. Simulations started in the 1950 to 1960 time period and were adjusted (calibrated) to match observed groundwater plumes in 2005/2006. The models were then used to simulate potential plume status up to the year 2038.

The following steps were included in the calibration of the fate and transport model:

- 1) Using the calibrated flow model to account for groundwater flow conditions for the periods of interest;

- 2) Using chlorobenzene as key constituent to develop the model due to the breadth and detailed coverage of the chlorobenzene database;
- 3) Compiling source data to determine size, strength, and temporal patterns in source concentrations;
- 4) Entering source concentration vs. time data in the fate and transport model;
- 5) Building a database of observed concentration data for the calibration period (2005/2006);
- 6) Running the entire model (flow model + fate and transport model) from 1950 to 2003 (period when the GMCS was not active);
- 7) Taking the resulting 2003 plume concentrations and entering these concentrations in a new model for the 2003 to 2005/2006 timeframe (period when the GMCS was active);
- 8) Comparing the modeled concentrations to observed concentrations;
- 9) Changing the model parameters in an attempt to improve the match; and
- 10) Repeating steps 3-9 for other constituents of concern: 1,4-dichlorobenzene (DCB), 2,4-dichlorophenoxyacetic acid (2,4-D), tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (1,2-DCE), and vinyl chloride (VC).

Key results from the calibration efforts for the model are summarized below:

- Historical industrial and highway dewatering activities have had significant effects on the distribution of the observed contaminant plumes today;
- Due to a lack of detailed flow records for industrial and highway dewatering wells, it is impossible to match the current observed plumes precisely. Nevertheless, a model that generally matched the key features of the groundwater plumes was constructed. This model can be used to meet the objectives presented earlier.
- Calibration efforts focused on evaluating the model response to a number of variables, including dispersivity (related to groundwater mixing), biodegradation rates, source decay rates, infiltration, industrial pumping well location and pumping rates, and highway dewatering well flowrates over time. After evaluating these parameters, a “Base Case” was developed that represented the best match that was achieved by manipulation of model variables.
- Key features of the existing chlorobenzene plume were matched with the model. These features included i) higher observed concentrations associated with the Krummrich, SA1, and SA2 source zones and sources associated with Clayton Chemical; ii) a portion of the Deep Hydrogeologic Unit (DHU) chlorobenzene dissolved plume extending to the northern portion of Site P, north of the main source zone; and iii) the Site R plume and portions of other plumes being captured by the GMCS.
- When all modeled constituents were included, over 94% of the total plume mass flux (mass discharge rate) is predicted to be captured by the GMCS. There is considerable variation in the capture rate for each constituent. For example:

- Approximately 99% of the total 2,4-D mass flux (~11,000 kilograms per year) is predicted to be captured by the GMCS in 2038.
- Approximately 91% of the vinyl chloride is predicted to be captured by the GMCS in 2038.
- Approximately 88% of the chlorobenzene mass flux is predicted to be captured by the GMCS in 2038.
- Although only 48% of the trichloroethene mass flux is predicted to be captured by the GMCS in 2038, this is a comparatively small plume compared to the mass flux of the other constituents (total mass flux of 17 kilograms per year of TCE going to the river or the GMCS compared to ~21,000 kilograms per year for all seven constituents).

When the highway dewatering system in East St. Louis is shut down as planned in 2010, groundwater flow from the aquifer to the river will increase, increasing the overall mass flux to the river. Eventually, however, the mass flux to the river will decrease as the effects of slow source decay overcome the effects of increased river discharge. By the time the system reaches steady state (about 2020), the mass flux to the river will be decreasing steadily and will continue to decrease as the source is depleted.

- Overall, the model likely presents a conservative estimate of actual conditions present at the site. For example,
 - The model predicts the presence of chlorobenzene in some portions of the Middle Hydrogeologic Unit (MHU) where the actual plume data shows no plume (see Part 2 Section 5).
 - Based on calibration results, the model uses a lower (slower) biodegradation rate than the Illinois Tiered Approach to Corrective Action Objectives (TACO) (35 IAC 742) standard.
 - Maximum detected concentrations from 1980s to 2006 were used to calculate source concentrations over time for the slow source decay term. For some constituents, this resulted in higher 2006 concentrations than actual measured values.

See Section 6.3 of Part 2 for a detailed discussion of the mass flux/capture rate calculations and results.

Part 1: Regional Groundwater Flow Model

American Bottoms Aquifer



Submitted to:

Mr. Steve Shroff, URS Corp.

April 14, 2008

Groundwater Services, Inc.
2211 Norfolk, Suite 1000, Houston, TX 77098

DEVELOPMENT OF A REGIONAL GROUNDWATER FLOW MODEL

FLOW MODEL EXECUTIVE SUMMARY

Background and Objectives

The southern portion of the American Bottoms aquifer is or has the potential to be affected by constituents originating from several facilities and waste management sites. Although several previous modeling efforts have focused on the American Bottoms aquifer, there was no single integrated flow and fate and transport model that could evaluate all sites of interest on a regional scale.

Groundwater Services, Inc (GSI) was retained by URS Corporation to develop a regional groundwater flow and fate and transport model covering the southern portion of the American Bottoms aquifer. This area includes the Sauget Area 1 (SA1) sites, the Sauget Area 2 (SA2) sites, and the Krummrich facility (Krummrich) in and around the Village of Sauget and the Village of Cahokia in St. Clair County, Illinois. Other sites of interest include ConocoPhillips East St. Louis Terminal and Clayton Chemical.

The objectives of this modeling project, as stated in the Groundwater Modeling Plan (GSI, 2006), were to upgrade/enhance the GSI 2001-2005 groundwater model into a regional model encompassing the Sauget/Cahokia areas such that

- 1) the modeled flow paths can be validated using actual plume measurements made during the RI phase;
- 2) a sensitivity analysis can be performed to assess how groundwater flow and contaminant nature and extent respond under various remedial alternatives during the FS phase;
- 3) the capture zone of the Sauget Area 2 GMCS can be further defined; and
- 4) the vertical mass flux of chemicals can be evaluated from both a site-specific and a regional perspective.

Results

The MODFLOW groundwater flow model was developed using data from previous hydrogeologic characterization projects, existing groundwater models, and new data developed as part of the SA1, SA2, and Krummrich site investigations. The groundwater model was then calibrated so that the simulated water levels in the model were representative of several actual potentiometric (water level) maps of data collected in 1962, 1990, and 2005. During calibration, model inputs such as river conductance, boundary conditions, pumping rates from wells, Mississippi River stage, and hydraulic conductivity were adjusted to reduce the difference between measured and simulated groundwater levels.

The final model simulates the regional aquifer system with an overall root mean squared (RMS) error of 0.7 ft and mean residual (MR) error of 0.06 ft for the model calibration to July 2005 water level data. Individual RMS errors of 0.8 ft, 0.6 ft, and 0.6 ft were obtained for the Shallow Hydrogeologic Unit (SHU), Middle Hydrogeologic Unit (MHU), and Deep Hydrogeologic Unit (DHU), respectively. Individual MR errors of 0.1 ft, 0.01 ft, and – 0.06 ft

April 14, 2008



were obtained for the SHU, MHU, and DHU, respectively. These RMS error values indicate that, in general, simulated water levels closely match actual water levels.

This report describes the development and calibration of the flow portion of the model. Model runs that will meet the objectives outlined above are described in Part 2 of the report.

1.0 INTRODUCTION

As requested by URS Corporation (URS), GSI Environmental Inc. (GSI), formerly known as Groundwater Services, Inc., has developed a regional groundwater flow model of the southern portion of the American Bottoms aquifer.

2.0 AREA DESCRIPTION

The study area includes portions of East St. Louis, the Village of Cahokia, and the Village of Sauget in St. Clair County. Sauget Area 1 (SA1) is located in Sauget and Cahokia and consists of five fill areas (Sites G, H, I, L, and N), one former borrow pit (Site M), and five segments of Dead Creek (CS-B through F) (Roux, 2001). Sauget Area 2 (SA2) consists of five sites: Sites O, P, Q, R, and S. Site R is a capped area approximately 2000 ft wide (parallel to the Mississippi River) and 500 ft long (perpendicular to the Mississippi River) and is currently being controlled by a Groundwater Migration Control System (GMCS) consisting of a 3300 ft long vertical barrier and three groundwater recovery wells. The W.G. Krummrich (Krummrich) facility is located entirely in the Village of Sauget. Other sites of interest include Clayton Chemical. Figure 1 shows the overall model domain.

3.0 HYDROGEOLOGIC CHARACTERIZATION

The geology of the area consists of unconsolidated valley fill deposits (Cahokia Alluvium) overlying glacial outwash material (Henry Formation) (Roux, 2001; GSI, 2001-2005). In general, the permeability of the unconsolidated material increases with depth with the outwash material being comprised of medium- to coarse-grained sand and gravel. These unconsolidated deposits are underlain by limestone and dolomite bedrock.

The available site data and technical references indicate that the unconsolidated water-bearing unit can be divided into three hydrogeologic units: the Shallow Hydrogeologic Unit (SHU; generally 15-30 ft deep), the Middle Hydrogeologic Unit (MHU; generally 30-70 ft deep), and the Deep Hydrogeologic Unit (DHU; generally 70-110 ft deep) (Figure 2).

The Shallow Hydrogeologic Unit is the only layer used in the model that acts as a confining layer. There are no aquitards or confining layers in the Middle or Deep Hydrogeologic Units.

4.0 PREVIOUS MODELS

Although several previous efforts to model the groundwater flow and/or transport of contaminants in and around the modeled area have been made, there is no detailed regional model capable of modeling both regional groundwater flow and contaminant fate and transport.

To date, three groundwater models have been developed that include all or portions of the modeled area. Brief descriptions and limitations of these models are listed below:

- Geraghty and Miller (1993): Local model near Site R. Includes both steady-state and transient calibration. Key limitations: no contaminant transport and 250 ft by 250 ft grid cell resolution in the vicinity of Site R.
- Clark (1997): Regional model of entire American Bottoms aquifer (14.5 miles by 29.5 miles). Steady-state calibration. Key limitations: single layer, no contaminant transport, and 0.5 mile by 0.5 mile grid cell resolution.
- GSI (2001-2005): Regional model with special focus on area near Sauget Area 2. Includes both flow and contaminant transport models. Includes detailed river bathymetry and SA2 GMCS. Key limitations: steady-state calibration only and calibration focused only on area of Sauget Area 2.

5.0 MODEL OBJECTIVES

The objectives of this study, as stated in the Groundwater Modeling Plan (GSI, 2006), were to upgrade/enhance the GSI 2001-2005 groundwater model into a calibrated regional model such that:

- 1) the modeled flow paths can be validated using actual plume measurements made during the RI phase;
- 2) a sensitivity analysis can be performed to assess how groundwater flow and contaminant nature and extent respond under various remedial alternatives during the FS phase;
- 3) the capture zone of the Sauget Area 2 GMCS can be further defined; and
- 4) the vertical mass flux of chemicals can be evaluated from both a site-specific and a regional perspective.

A numerical groundwater flow and contaminant transport model was developed using MODFLOW (McDonald and Harbaugh, 1988) and RT3D (Clement, 1997) to meet these objectives. This report describes the development and calibration of the flow portion of the model (Figures 1 through 48). Simulations to meet the objectives outlined above will be performed when the development and calibration of the contaminant transport model (RT3D) is completed.

6.0 MODEL DESCRIPTION

MODFLOW, developed by the U.S. Geological Survey (McDonald and Harbaugh, 1988), was used to simulate the flow of groundwater under baseline conditions and for various pumping scenarios. MODFLOW is a three dimensional, cell-centered, finite difference, saturated flow model that simulates both steady-state and transient groundwater flow. Visual MODFLOW Pro (Waterloo Hydrogeologic Inc.) was used as the pre and post processor and as the user interface to the MODFLOW 2000 model.

Key model attributes, assumptions, and input data for the MODFLOW model are listed below.

6.1 Model Grid

The model domain measured 8 miles by 8 miles (Figure 1). A non-uniform finite-difference grid with 60 ft by 60 ft cells in the vicinity of the SA2 GMCS was used with cell size gradually increasing with distance from Site R (Figures 3 and 4). Adjacent model cell column and row widths were not altered more than a factor of 1.5 (ASTM D 5880-95). This type of variable-size grid provides a good balance between simulation accuracy and run time.

6.2 Model Capabilities

The model was designed to evaluate the movement of constituent plumes from various source zones in the American Bottoms aquifer and the overlying shallow water-bearing unit. This section of the report summarizes the development of the flow portion of the groundwater model. Part 2 of this report shows results of model runs designed to meet the objectives outlined in Section 5.0.

6.3 Model Domain Boundary Conditions

The Mississippi River (discussed in detail in Section 6.5 below) served as the boundary condition on the western edge of the model. Constant head cells were used in the model to represent the eastern boundary of the model domain (the bluff line) based on “steady-state” constant head elevations used in the regional groundwater flow model developed by Clark (Figure 20 in Clark, 1997) and modified during the calibration process. Initial constant head boundaries ranged from 400 to 410 ft. Because flow is primarily east to west, the northern and southern boundaries of the model domain were represented as no-flow boundaries in all model layers (GSI, 2002b; Geraghty and Miller, 1993) (Figure 5).

6.4 Model Layers

The three hydrogeologic units at the site were each represented by a separate layer. The top layer, representing the SHU, consisted of an unconfined unit with a porosity of 0.30. The second layer, representing the MHU, consisted of a convertible confined/unconfined unit. The bottom layer, representing the DHU, was simulated as a confined unit. Geologic descriptions and hydraulic conductivity data indicate that the SHU can serve as a semi-confining layer for the deeper hydrogeologic units. As shown in Figure 2, the potentiometric surface of the MHU extends into the SHU (Layer 1 in model), also indicating confined or semi-confined conditions. No aquitards restrict vertical groundwater flow between the Middle and Deep Hydrogeologic Units.

Surface elevations for the top layer of the model (SHU, Layer 1 in the model) were obtained by combining ground surface elevations from existing boring logs (Table 1) with USGS digital elevation models (DEM) (Cahokia, Columbia, French Village, Granite City, Monks Mound, Millstadt in Illinois; and Webster Groves, Oakville, and Clayton in Missouri (<http://data.geocomm.com/dem/demdownload.html>)) and interpolating the combined data set using the nearest neighbor interpolation over the entire model domain (Figures 6 and 7). The interpolated data were imported into the model.

The bottom elevations of the SHU and the top elevations of the MHU (Layer 2 in the model) were established by Kriging stratigraphic elevation data from geologic cross-sections developed by URS (Drawing numbers 5, 6, and 7 in URS, 2001), Geraghty and Miller (Figure 3 in G&M, date unknown), Bergstrom and Walker (Figure 4 in Bergstrom and Walker, 1956), Schicht (Figure 7 in Schicht, 1965), Roux (Figure 2-1 in Roux, 2001), and boring log data available from the Supplemental Investigation (Table 1).

Bedrock elevations, which form the bottom of the lowest layer (DHU, Layer 3 in the model), were established by Kriging data contained in Bergstrom and Walker (Figure 2 in Bergstrom and Walker, 1956), results from a small-area geophysical study of an area near the Krummrich facility, and available boring log data (Table 1). The Kriged data were imported into the model.

The bottom elevation for the MHU was calculated by dividing the interpolated thickness between the SHU and bedrock into two layers of equal thickness. Figures 8 and 9 show the top elevations for the MHU while Figures 10 and 11 show the top elevations for the DHU. Figures 12 and 13 represent the bedrock elevations, which form the bottom of the model.

Figures 14 through 19 show the thickness of the SHU, MHU, and DHU in the model. Figure 20 represents a west-east cross-section through the model at the GMCS well EW-2.

6.5 Mississippi River

The Mississippi River was modeled using MODFLOW's river package. The areal extent of the river was obtained from USGS topographic maps and URS figures (Figure 21). Each river cell was assigned a river stage, river bottom elevation, and conductance. Conductance represents the resistance to flow caused by the riverbed between the river and the groundwater.

River stage was based on a gauging station near Site R, Station Number USGS 07010000 (Eads Bridge). The river stage was assumed constant for all river cells in the model.

River bottom elevations for each cell were based on 26 U.S. Army Corps of Engineers bathymetric cross sections (USACE, 2005), approximately 2200 ft apart on average, in the model domain (Figures 22 and 23). The river bottom profiles based on the cross sections are shown in Table 2.

Initially, each river cell was also assigned a constant conductance value. The riverbed conductance was derived from the average of monthly conductance estimates reported by Schicht (Table 29 in Schicht, 1965). The initial conductance for a 60 ft by 60 ft cell was 795 ft²/day. Proportionally higher conductances were used for cells with larger areas.

Final conductance values used in the model are discussed in detail in the calibration section (Section 7.4) of this report.

6.6 Hydraulic Conductivity

There were no maps available of the SHU hydraulic conductivity over the entire scale of the model. Therefore, initial hydraulic conductivity values for the SHU were based on modeling studies performed for the Sauget Area 1 EE/CA and RI/FS (GSI, 2001a), and existing cross

sections (see Section 6.4) that defined the upper and lower layer elevations. The initial hydraulic conductivity value used for the SHU near the site was 0.0005 cm/sec for horizontal hydraulic conductivity (K_x and K_y) and 1×10^{-6} cm/sec for the vertical hydraulic conductivity (K_z), based on previous GSI modeling work (GSI, 2002b) (Figure 24). Hydraulic conductivities in the SHU were assumed to be a single value across the model domain.

Values of hydraulic conductivity for the MHU and DHU were taken from a detailed analysis of American Bottoms aquifer test data (pump tests and specific capacity tests) performed by Schicht (1965) (Figure 23). Within the modeled area for this project, data from two pump tests (ranging from 1 to 4 days in length) and 31 specific capacity tests (from industrial, municipal, irrigation, and relief wells) were used. Schicht compared results from two pump tests located near the Sauget area and hydraulic conductivity values derived from the theoretically less accurate specific capacity tests and concluded that the hydraulic conductivity values from these two data sources were found to "agree closely." Contour lines from Schicht's map (Figure 23 in Schicht, 1965) were then kriged as part of this project to construct a detailed, continuous, spatially-varying distribution of hydraulic conductivity across the model domain (Figure 24) which was then imported into the model.

Vertical hydraulic conductivity values were used in the model to calculate leakance terms.

Final hydraulic conductivities used in the model are discussed in detail in the calibration section (Section 7) of this report.

6.7 Surface Infiltration

An initial surface infiltration rate of 7.8 inches per year was used throughout the entire model domain to represent infiltration from rainfall based on data from Schicht (Table 26 in Schicht, 1965); Geraghty and Miller (1993); Clark (1997); and GSI (2001-2005) (Figure 25).

Final surface infiltration values used in the model are discussed in detail in the calibration section (Section 7.4) of this report.

6.8 Highway Dewatering Projects

A regional pumping center, assumed to be withdrawing groundwater from all three layers, was established in the model to represent ongoing highway dewatering projects in the East St. Louis area (Ritchey and Schicht, 1982; Schicht and Buck, 1995). An initial pumping rate of 6250 gpm was used (Schicht and Buck, 1995). The highway dewatering pumping was terminated in 2010 during the fate and transport model development.

Final highway dewatering pumping rates used in the model are discussed in detail in the calibration section (Section 7.4) of this report.

6.9 GMCS System

The Sauget Area 2 GMCS was incorporated into the model. The GMCS system consists of a "U"-shaped slurry wall (3 ft wide, 3,300 ft long, 140 ft deep) (Solutia, 2002; URS, 2004) located between SA2 Site R and the Mississippi River and three groundwater extraction wells

between the slurry wall and Site R. A hydraulic conductivity of 1.4×10^{-8} cm/sec (Solutia, 2005) was used for the slurry wall extending from the SHU to the DHU in the model. The slurry wall was modeled using MODFLOW's Horizontal Flow Barrier package.

6.10 Porosity

An initial effective porosity value of 0.2 was used in the model based on data from the *Focused Feasibility Study Interim Groundwater Remedy Sauget Area 2 Sites O, Q, R, and S* (Solutia, 2002) and the *Source Evaluation Study* (GSI, 2001a). Effective porosity was adjusted during the contaminant transport model calibration. Final effective porosities used in the model are discussed in detail in the calibration section (Section 7) of this report.

6.11 Transient Flow – Storage Coefficients

Values of specific storage were based on pump test data from Schicht (Table 7, 1965) and aquifer tests from Geraghty and Miller (Tables 1 and 2, 1993).

Pumping test data analyzed by Schicht (1965) provided two storage coefficients (also called storativity; equal to the product of specific storage and aquifer thickness) values of 0.0011 and 0.002 based on early drawdown data before gravity drainage occurred. The mean of these two storage coefficient values of 0.0016 was used in the model, and corresponds to specific storage values of 9.41×10^{-5} ft⁻¹, 5.33×10^{-5} ft⁻¹, and 2.25×10^{-5} ft⁻¹ for the SHU, MHU, and DHU, respectively. A specific yield of 0.1 was used for the entire model domain.

6.12 Head Observation Wells

A total of 126 head observation wells were imported into the model at locations where heads were measured during the July 6-8, 2005 static water level survey for comparison of simulated to measured heads (Figure 26). The midpoint of the screen interval was used as the measurement point depth of the head observation wells.

7.0 MODEL CALIBRATION

Calibration is the process of adjusting model parameters until the difference between modeled outputs and site-specific data are reduced to an acceptable level.

Both qualitative and quantitative comparisons were made between the model and site-specific information. Qualitative flow comparisons included comparison of observed groundwater flow direction and plume geometry to the simulated flowpaths. Quantitative flow model comparisons included the comparison of simulated heads to measured heads and a comparison of the residual differences between the two.

Quasi-steady-state calibration was performed to compare model output to pre-GMCS potentiometric surface maps. Regional maps developed by Schicht (Figure 54 in Schicht, 1965) and Schicht and Buck (Figure 14 in Schicht and Buck, 1995), were used for a regional calibration. Potentiometric surface maps from 2002 and 2005 were used for a more detailed calibration in the Site area.

The model was calibrated in the sequence described in the following sections.

7.1 1962 Semi-Qualitative Comparison

Initially the model was compared to the 1962 Schicht (Figure 54 in Schicht, 1965) potentiometric surface map. The model was run in steady-state mode using a constant river stage of 400 ft MSL to match the 1962 stage (Schicht, 1965).

Initial calibration runs indicated that the predicted static water levels from the MHU were considerably higher than the measured values. Decreasing the constant river constant conductance values by half did not improve the discrepancies between the measured and calculated water levels.

Better agreement between simulated and measured heads was achieved by varying the conductance along the river. For this purpose, variable conductance values were calculated based on an assumed river bed thickness (T) of 10 ft, river bed hydraulic conductivity (K) values used by Clark (1997) (Table 3), and length (L) and width (W) of the model cell representing the river. Conductance for each model river cell was then calculated using the formula:

$$\text{Conductance} = K \times L \times W/T$$

Varying the river conductance resulted in a simulated head value of 351 ft MSL for the deepest cone of depression compared to the measured value of 346 ft MSL (Figures 27 and 28), which was a significant improvement compared to the initial differences in modeled and measured heads.

Note that the shape of Schicht's 1962 drawdown cone (Figure 54 in Schicht, 1965), and more importantly Schicht's hydraulic conductivity (Figure 23 in Schicht, 1965) do not indicate the presence of highly permeable fluvial deposits parallel to the river. A high degree of heterogeneity parallel to the river would have likely expressed itself as a more egg-shaped cone of depression (narrow in the north-south direction and thicker in an east-west direction). Schicht's figure indicate heterogeneity in the form a kidney-shaped high-conductivity zone in the MHU and DHU near the Krummrich facility and extending to the southeast (Figure 23 in Schicht, 1965). This heterogeneity feature was incorporated into the model (Figure 24).

7.2 1990 Semi-Qualitative Comparison

Following initial calibration to the 1965 head data, the model was compared to the 1990 Schicht and Buck potentiometric surface (Schicht and Buck, 1995). The model was run in steady-state mode using a river stage of 384.8 ft MSL to match the stage used by Schicht and Buck.

As in the 1962 comparison, calibration runs showed that the predicted static water levels from the MHU were considerably higher than the measured values. A better match was achieved by: a) lowering the water level in constant head cells at the eastern boundary of the model domain by 2 ft; b) adding the Cahokia Canal south of the Site to the model; and c) adding the Frank Holten State Park Lake east of the Site to the model. These features were incorporated into the MODFLOW model developed by Clark (1997).

The Cahokia Canal was modeled using the MODFLOW River package with a conductance value based on a river bed thickness of 5 ft, river bed conductivity of 1.6×10^{-3} cm/sec (the geometric mean of all the Mississippi River bed conductivity values in the model domain), bottom elevations of 372-373 ft MSL based on the Clark model (Clark, 1997), and an initial stage 2 ft below the ground surface.

The Frank Holten State Park Lake was modeled as a general head boundary using a conductance value based on a sediment bed thickness of 10 ft, bed conductivity of 1.6×10^{-3} cm/sec (the geometric mean of all the Mississippi River bed conductivity values in the model domain, Table 3), and an initial stage 1 ft below the ground surface.

A better match between the measured and calculated water levels was obtained by using a stage ranging from 392 to 399 ft MSL for the Cahokia Canal and a stage of 407 ft MSL for the lake.

The November 1990 potentiometric surface map was developed from data taken when the Mississippi River stage was fairly low, around 385 ft MSL. This value was selected as it covered the entire model area and was relatively recent. This comparison indicated good relative agreement, as the general shape and values of the predicted potentiometric surface were similar to the reported potentiometric surface (including the cone of depression caused by the highway dewatering system). The predicted values did not provide an absolute match to the observed values due to differences in river stage. However, a modeled value of 370 ft MSL for the deepest cone of depression was obtained compared to a measured value of 375 ft MSL (Figures 29 and 30). Overall, the MODFLOW groundwater flow model was considered to yield a reasonable simulation of the aquifer system.

7.3 2002 Qualitative Comparison

The model was next compared to the September 23, 2002 potentiometric surface map (URS, Fig 5-9b, 2004). An initial flow calibration against water levels was performed by adjusting the Mississippi River stage to 384 ft MSL to match the stage on September 23. The model was run in steady-state and the predicted values were qualitatively compared to the measured values.

Initial calibration runs showed that the predicted static water levels were lower than the actual values measured (Figures 31 and 32). However, the Mississippi River Stage varied significantly in the month prior to the collection of water levels at the Site (stage values ranged from a high of 393 ft MSL on August 25, 2002, to a low of 383 ft MSL on September 22, 2002, the day before the sampling event). Since the steady-state model assumes a constant stage, the model was not able to reproduce the effects of the varying river stage.

7.4 2005 Quantitative Comparison

The final flow calibration was against water levels measured on July 6-8, 2005 by URS. First, the Mississippi River stage was adjusted to 390.12 ft MSL and the GMCS pumping rates to 675, 658, and 646 gpm, respectively for EW-1, EW-2, and EW-3. The model was run in steady-state mode and the predicted values compared to the measured values.

April 14, 2008



Initial calibration runs showed that the predicted static water levels were considerably higher than the measured values. Since the pumping rates of the GMCS system and the Mississippi River Stage were not constant over the period of the sampling event, an improvement in the agreement between measured and calculated water levels was achieved by: a) running the model in transient mode; b) adjusting Layer 1 hydraulic conductivity; and c) adjusting Site R hydraulic conductivity and recharge.

Conversion of the model from steady-state to transient was achieved by using Mississippi River stages and GMCS pumping rates ranging from May 6 to July 8, 2005. For this purpose, weekly averages of the river stage and pumping rates were obtained from May 6 through July 1 and daily rates from July 1 through July 8:

Model Simulation Day	Date	EW-1 Pumping Rate (gpm)	EW-2 Pumping Rate (gpm)	EW-3 Pumping Rate (gpm)	Surface Water Level (ft MSL)	Notes
0	5/6/2005	491	490	279	390	Daily rate
7	5/13/2005	750	744	562	387	Weekly averaged rate
14	5/20/2005	192	204	109	393	Weekly averaged rate
21	5/27/2005	250	248	111	393	Weekly averaged rate
28	6/3/2005	508	512	223	390	Weekly averaged rate
35	6/10/2005	287	279	88	393	Weekly averaged rate
42	6/17/2005	12	57	0	399	Weekly averaged rate
49	6/24/2005	34	173	1	395	Weekly averaged rate
56	7/1/2005	50	139	18	392	Weekly averaged rate
57	7/2/2005	0	223	0	391	Daily rate
58	7/3/2005	0	226	0	391	Daily rate
59	7/4/2005	0	242	0	391	Daily rate
60	7/5/2005	0	525	0	391	Daily rate
61	7/6/2005	1	710	1	391	Daily rate
62	7/7/2005	386	703	372	390	Daily rate
63	7/8/2005	675	658	646	390	Daily rate

Mississippi River

The riverbed conductance was increased by a factor of 12 to improve the comparison between simulated and measured groundwater heads. This increase resulted in a better distribution of mean of residual errors for the groundwater heads.

Effects of a transient river stage were studied during the calibration process (Section 5 of Part 2) and the analysis indicated that the fluctuating river stage did not significantly affect the regional groundwater flow patterns or the accuracy of the model calibration. Therefore, a constant river stage of 390 ft MSL was retained for all subsequent modeling runs.

Porosity

Although effective porosities ranging from 0.2 to 0.33 for the SHU and 0.1 to 0.24 for the MHU and DHU were applied to the model, better agreement between simulated and measured concentrations was achieved by using an effective porosity of 0.3 for the SHU and 0.18 for the MHU and DHU.

Infiltration Rate

Although, a recharge rate of 7.3 in/yr resulted in an overall RMS error of 0.7 ft and a MR error of 0.001 ft, subsequent calibration of the contaminant transport model (Section 5 of Part 2) yielded better results with a recharge rate of 7.8 in/yr. Therefore, a final recharge rate of 7.8 in/yr was retained in the flow model.

Highway Dewatering Projects

A regional pumping center, assumed to be withdrawing groundwater from all three layers in proportion to hydraulic conductivity, was established in the model to represent ongoing highway dewatering projects in the East St. Louis area (Olson and Sanderson, 2000; Schicht and Buck, 1995; Collins and Richards, 1986; Ritchey and Schicht, 1982; Emmons, 1979; Baker, 1972; Reitz, 1968; and Schicht and Jones, 1962). Based on information contained in the references cited above, an initial pumping rate of 6250 gpm was estimated to be representative of the dewatering projects.

During the calibration of the contaminant transport model, the pumping rates of the Highway Dewatering wells were increased from 6250 gpm to a total of 6828 gpm to improve the calibration of the contaminant plumes (Section 5.4 of Part 2). Based on personal communication with Solutia Inc., highway dewatering pumping was assumed to terminate in 2010 due to planned road construction projects.

Historical Industrial Wells

Ranney Wells

- Initially, the modeling effort focused on three high-capacity Ranney-type wells, one located near the Mississippi River and Site R (Monsanto, date unknown_a), and two on the Krummrich facility (Personal communication, 2007; Ecology and Environment, 1988; Midwest Rubber, 1969, and Monsanto, date unknown_b).
- Based on historical engineering drawings (Monsanto, date unknown_a,b), the two Krummrich Ranney-type wells were simulated with pumping from five model grid cells to account for the multiple laterals under and north of the Plant (Figure 33).
- Similarly, the River/Site R Ranney-type well was simulated with pumping from five model cells to account for the laterals near and under the Mississippi River.
- During the calibration of the transport model, two of the five cells used to simulate the Krummrich Ranney-type wells were turned off to improve the calibration of the groundwater plumes (Figure 33) (Section 5 of Part 2). Turning these two cells off prevented the model cells from drying and becoming inactive in the Krummrich Plant vicinity.
- Final wells and pumping rates used in the model are discussed in detail in the calibration section (Section 5.4 of Part 2) of this report.

Other Industrial Wells

- Based on the Illinois State Water Survey Division historical groundwater model (Schicht et al., 1984a-b; Ritchey et al., 1984c-e), seven other historical industrial wells located in

the model domain (Figure 33) were incorporated into the model during the calibration process in an attempt to improve the calibration.

- However, no significant improvement in the model calibration was observed after incorporating these wells (Section 5.3.7 of Part 2), and because this model required a longer running time than the base case (incorporating only the Ranney-type industrial wells), the base case model was retained.
- Final wells and pumping rates used in the model are discussed in detail in the calibration section (Section 5.4 of Part 2) of this report.

Shallow Hydrogeologic Unit Calibration

The initial horizontal hydraulic conductivity (K_x and K_y) value used for the SHU (Layer 1 in the model) near the site was 0.0005 cm/sec, which was taken from previous GSI modeling studies (GSI, 2002b). Better agreement between modeled and measured heads was achieved by increasing both the horizontal and vertical hydraulic conductivity arrays in the model. The horizontal hydraulic conductivity was increased to 5×10^{-3} cm/sec, and the vertical hydraulic conductivity was increased to 5×10^{-5} cm/sec to better match measured heads in this unit. Slug test data collected by URS supported the use of an increased horizontal hydraulic conductivity. More detailed SHU horizontal and vertical hydraulic conductivity data will be developed for specific sites of interest during the development of the contaminant transport model.

Additionally, the hydraulic conductivity of the SHU in the area of Site R was decreased to 1×10^{-8} cm/sec for all K_x , K_y , and K_z to reflect the presence of the cap over Site R. The recharge over this area was also decreased to 0 in/yr.

These changes resulted in a good agreement between the measured and calculated water levels with a root mean square (RMS) error of 1.0 ft for the SHU. However, monitoring wells B-22A, B-24A, and B-28A were not considered in the analysis due to their close proximity to the slurry wall and Site R (the model could not reproduce these heads accurately), while well B-29A was not considered due to its location on the very edge of Site R.

Middle and Deep Hydrogeologic Unit Calibration

The hydraulic conductivity map developed by Schicht in 1965 was used to obtain values of the horizontal hydraulic conductivity for the Middle and Deep Hydrogeologic Units (Layers 2 and 3 in the model) (K_x and K_y ; no anisotropy is assumed in the horizontal plane). A vertical hydraulic conductivity (K_z) of 50% of K_x and K_y was used for all zones in both the Middle and Deep Hydrogeologic Units. Using these values of hydraulic conductivity, a final RMS error of 0.7 ft was obtained for the MHU and 0.7 ft for the DHU.

7.5 Final Calibration Results

In accordance with ASTM Standard D5490-93, both qualitative and quantitative measurements were used to determine the sufficiency of model calibration. On a qualitative basis, the general shape of the potentiometric surface was reproduced by the calibrated model, indicating that the boundary conditions and layer parameters likely simulate the physical boundaries controlling

groundwater flow within the model domain. As explained in Section 7.2 above, although the model slightly over-predicts heads in the aquifer, the over-prediction is caused by the varying head in the Mississippi River, which cannot be reproduced in a steady-state model. Although the steady-state heads are higher than the average heads measured in July 2005, the heads are representative of annual average conditions within the aquifer.

Figures 34 through 42 show the modeled and measured potentiometric surfaces for the three hydrogeologic units in the model. Spatial correlation of the computed versus simulated water level residuals at individual wells are shown in Figures 43 through 45. Scattergrams of the computed versus simulated water levels are shown in Figures 46 through 49.

As recommended in ASTM standard D-5490-93, residual statistics and second-order statistics, both quantitative measures, were also used to assess the sufficiency of the model calibration. Both of these methods rely on calculated residuals, which are the difference between measured and simulated values of hydraulic head at specific well locations:

$$r_i = h_i - H_i$$

where:

- r_i = residual at location i ;
- h_i – computed head at location i ;
- H_i = measured head at location i .

Positive residuals indicate that computed heads are greater than measured heads, while negative residuals indicate the opposite. As recommended by ASTM standard D-5490-93, the maximum, minimum, and arithmetic mean residuals were calculated, and these are reported in Table 5. Overall residuals ranged from 2.14 ft above the measured head at SA-Q-1 to 0ft below the measured head at TCMW-5-S. These results, along with the residual mean of 0.06, indicate that the model is very slightly biased towards higher hydraulic heads as discussed in Section 7.2 above.

Because negative and positive residuals cancel each other out, the residuals reported above are useful for indicating bias, but not particularly useful in assessing the overall sufficiency of model calibration. Second-order statistics provide a better indication of overall model calibration and an indication of the goodness-of-fit to the measured head data because they are based on the absolute value of the residuals so that negative and positive values do not cancel each other out. The two second-order statistics used to assess calibration sufficiency were the standard deviation of residuals (recommended by ASTM D-5490-93) and a commonly-used measurement employed by groundwater professionals, the root mean square (RMS) error. The standard deviation of residuals is:

$$s = \left(\frac{\sum_{i=1}^n (r_i - R)^2}{n - 1} \right)^{1/2}$$

where s is the standard deviation of residuals, R is the mean of the residuals and n is the number of residuals. Low values of s indicate good fit of the predicted heads to measured heads, while larger values indicate an increasingly poor fit. The value of s for the shallow, middle, and lower hydrogeologic units were 0.76, 0.60, and 0.63, respectively. The value of s for all of the layers combed was 0.68. These values are within the range of 0.7 to 1 suggested by Spitz and Moreno (1996) as indicating adequate model calibration.

RMS errors were calculated as follows:

$$RMS = \left(\sum_{i=1}^n \frac{(r_i - R)^2}{n} \right)^{1/2}$$

An RMS error of 0 indicates a perfect match between predicted and measured heads, and increasing values of RMS indicate an increasingly poor match of predicted to measured heads. RMS errors for the shallow, middle, and deep hydrogeologic layers were 0.77, 0.59, and 0.62, respectively, with an overall RMS of 0.68 for all layers combined.

Although there are no criteria for determining when a model is adequately calibrated based on RMS values, Zheng and Bennett (1995) suggest that the RMS error can be normalized by dividing it by the difference between the maximum and minimum measured heads to get a crude statistic indicating how the residuals compare to the range of measured heads. The overall difference between the maximum and minimum heads measured in July 2005 is 11.40 ft. The RMS errors of the three individual hydrogeologic layers and the overall RMS range from approximately 5% to 7% of this maximum head difference, indicating that the calibration errors are a small fraction of the measured head differences across the model domain.

The qualitative and quantitative measurements of model calibration indicate that the preliminary model calibration is slightly biased high because of Mississippi River head variations, but that the calibrated model meets general criteria for acceptance.

The final modeling results are based on the best estimates of input parameters, model discretization, boundary conditions, sensitivity studies of the effects of model parameters on predictive model outcomes, and other factors.

8.0 SENSITIVITY ANALYSIS

Sensitivity analyses are performed on calibrated groundwater models to identify the input parameters that have the most impact on the calibration and simulation results. In accordance with ASTM standard D 5611-94, a sensitivity analysis was performed after the completion of the development and calibration of the contaminant transport model. The sensitivity analysis is discussed in detail in Section 7 of Part 2.

9.0 MODEL LIMITATIONS

The model has the following key limitations:

- the Shallow Hydrogeologic Unit is assumed to have a constant hydraulic conductivity.
- the river is simulated with idealized cross section and river bottom conductance values.
- the model has some difficulty precisely matching observed water levels in four the piezometers immediately adjacent the GMCS and Site R.

April 14, 2008

10.0 FINAL MODEL PARAMETERS

Final Model Parameters

Parameter	Hydrogeologic Unit or Boundary	Value	Units	Source
General				
Model domain dimensions	N/A	64	mi ²	Model design
Maximum grid cell dimension	N/A	Variable: 60 - 580	ft	Model design
Layer Properties				
Horizontal hydraulic conductivity	SHU	5×10^{-3}	cm/s	Initial – GSI (2002b) Adjusted during calibration.
	SHU, Site R Cap	1×10^{-8}	cm/s	Initial – GSI (2002b) Adjusted during calibration.
	MHU and DHU	Variable: 0.07 – 0.14	cm/s	Schicht (1965)
Vertical hydraulic conductivity	SHU	5×10^{-5}	cm/s	Initial – GSI (2002b) Adjusted during calibration.
	SHU, Site R Cap	1×10^{-8}	cm/s	Initial – GSI (2002b) Adjusted during calibration.
	MHU and DHU	Variable: 0.035 – 0.07	cm/s	GSI (2002b)
Specific storage	SHU	9.41×10^{-5}	ft ⁻¹	Schicht (1965)
	MHU	5.33×10^{-5}	ft ⁻¹	Schicht (1965)
	DHU	2.25×10^{-5}	ft ⁻¹	Schicht (1965)

April 14, 2008

Parameter	Hydrogeologic Unit or Boundary	Value	Units	Source
Specific yield	All	0.1		Schicht (1965)
Porosity	SHU MHU/DHU	0.3 0.18		Initial – Solutia (2002); GSI (2001a) Adjusted during calibration of transport model
Recharge rate	SHU	7.8	in/yr	Schicht (1965); Geraghty and Miller (1993), Clark (1997), GSI (2001-2005)
	SHU, Site R	0	in/yr	Adjusted during calibration
Boundaries				
Stream Conductance	Mississippi River (60 x 60 cell)	11,700	ft ² /d	Initial – Schicht (1965) Adjusted during calibration
	Cahokia Canal (580 x 580 cell)	307051	ft ² /d	Adjusted during calibration
	Frank Holten State Park Lake (60 x 580 cell)	21176	ft ² /d	Adjusted during calibration
Stream stage	Mississippi River	Variable: 387 - 399	ft MSL	Initial – Schicht (1965) Adjusted during calibration
	Cahokia Canal	Variable: 392 - 399	ft MSL	Initial – Clark (1997) Adjusted during calibration
	Frank Holten State Park Lake	407	ft MSL	Initial – Clark (1997) Adjusted during calibration
Mississippi River Bottom Elevation	All	Variable:	ft MSL	USACE (2005)
GMCS slurry wall hydraulic conductivity	All	1.4×10^{-8}	cm/s	Solutia (2002); URS (2004)
Pumping Wells				
EW-1		Variable:	gpm	URS Corporation (2006)

April 14, 2008

Parameter	Hydrogeologic Unit or Boundary	Value	Units	Source
		0 - 750		
EW-2		Variable: 0 - 744	gpm	URS Corporation (2006)
EW-3		Variable: 0 - 646	gpm	URS Corporation (2006)
Highway dewatering wells		6,828	gpm	Initial – Ritchey and Schicht (1982); Schicht and Buck (1995) Adjusted during calibration

Notes:

cm/s = centimeters per second

d = day

ft = feet

gpm = gallons per minute

in/yr = inches per year

mi = mile

MSL = mean sea level

11.0 REFERENCES

- American Society for Testing and Materials, 1998. "Standard Guide for Conducting a Sensitivity Analysis for a Ground-Water Flow Model Application", ASTM D 5611-94, Philadelphia, PA.
- American Society for Testing and Materials, 1998. "Standard Guide for Comparing Ground-Water Flow Model Simulations to Site-Specific Information", ASTM D 5490-93, Philadelphia, PA.
- American Society for Testing and Materials, 2000. "Standard Guide for Subsurface Flow and Transport Modeling", ASTM D 5880-95, Philadelphia, PA.
- Bergstrom, R.E. and T.R. Walker, 1956. *Groundwater Geology of the East St. Louis Area, Illinois*, Illinois State Geological Survey, Urbana, Illinois.
- Clark, G.R., 1997. *American Bottoms Regional Ground-Water Flow Model*, Illinois Department of Natural Resources, Office of Water Resources, Springfield, Illinois.
- Clement, T.P. 1997. *RT3D - A Modular Computer Code for Simulating Reactive Multi-Species Transport in 3-Dimensional Groundwater Aquifers*. Pacific Northwest National Laboratory, Richland, WA, USA. PNNL-11720
- Geraghty and Miller, 1993. "Development of a Three-Dimensional Ground-Water Flow Model for Sauget Site R, Sauget, Illinois", Plainview, New York, February, 1993.
- Groundwater Services, Inc., 2001a. "Source Evaluation Study", Prepared for Solutia Inc. by Groundwater Services, Inc., Houston, Texas, May 21, 2001.
- Groundwater Services, Inc. 2001b. "Hydraulic Containment Study", Prepared for Solutia Inc. by Groundwater Services, Inc., Houston, Texas, June 20, 2001.
- Groundwater Services, Inc. 2001c. "Discharge Control Study", Prepared for Solutia Inc. by Groundwater Services, Inc., Houston, Texas, November 29, 2001.
- Groundwater Services, Inc. 2002a. "Mass Containment Study", Prepared for Solutia Inc. by Groundwater Services, Inc., Houston, Texas, January 24, 2002.
- Groundwater Services, Inc., 2002b. "Interim Groundwater Remedy Design Basis" in "Focused Feasibility Study Interim Groundwater Remedy Sauget Area 2 Sites O, Q, R and S", Solutia Inc., St. Louis, Missouri, March 31, 2002.
- Groundwater Services, Inc., 2002c. "Preliminary results of volatile organic compound and semi volatile organic compound groundwater transport analysis and comparison to ecological benchmark, W.G. Krummrich Plant, Sauget, Illinois" in "Focused Feasibility Study Interim Groundwater Remedy Sauget Area 2 Sites O, Q, R and S", Prepared for Solutia Inc. by Groundwater Services, Inc., Houston, Texas, November 25, 2002.
- Groundwater Services, Inc. 2003a. "Sauget Area 2 Focused Feasibility Study", Prepared for URS Corp. by Groundwater Services, Inc., Houston, Texas, November 20, 2003.
- Groundwater Services, Inc. 2003b. "Sauget Area 2 Site R MODFLOW Model Calibration", Prepared for Solutia Inc. by Groundwater Services, Inc., Houston, Texas, November 24, 2003.
- Groundwater Services, Inc. 2004. "Physical and Chemical Properties – DNAPL Characterization Study", in "RCRA Corrective Measures Study (CMS) Solutia Inc. W. G. Krummrich Facility Sauget, Illinois". Prepared for Solutia Inc. by Groundwater Services, Inc., Houston, Texas, August 27, 2004.
- Groundwater Services, Inc. 2005. "Results of DNAPL Characterization and Remediation Study", Prepared for Solutia Inc. by Groundwater Services, Inc., Houston, Texas, January 21, 2005.
- Groundwater Services, Inc. 2006. "Groundwater Modeling Plan", Prepared for URS Corporation by Groundwater Services, Inc., Houston, Texas, March 27, 2006.

- McDonald, M.G. and A. Harbaugh, 1988. *A Modular Three Dimensional Finite-Difference Groundwater Flow Model*, Techniques of Water Resources Investigations 06-A7, USGS.
- Ritchey, J. D. and R.J. Schicht, 1982. "Ground-Water Management in the American Bottoms, Illinois," State, County, Regional, and Municipal Jurisdiction of Ground-Water Protection, Proceedings of the Sixth National Ground-Water Quality Symposium, Atlanta, Georgia, September 14-22, 1982, National Water Well Association.
- Roux Associates, Inc. 2001. "Engineering Evaluation/Cost Analysis Remedial Investigation/Feasibility Study Sauget Area 1 Sauget and Cahokia, Illinois", Prepared for Solutia Inc. by Roux Associates, Inc., Houston, Texas, June 9, 2001.
- Schicht, R.J., 1965. *Ground-Water Development in East St. Louis Area, Illinois, Report of Investigation 51*, Illinois State Water Survey, Urbana, Illinois.
- Schicht, R.J. and A. G. Buck 1995. *Ground-Water Levels and Pumpage in the Metro-East Area, Illinois, 1986-1990*, Illinois State Water Survey, Urbana, Illinois.
- Solutia, 2002, "Focused Feasibility Study Interim Groundwater Remedy Sauget Area 2 Sites O, Q, R, and S," Solutia, Inc., March 31, 2002.
- Solutia, 2005, "Interim Operating Period 1 Tech Memo," Solutia, Inc., April 1, 2005.
- Spitz and Moreno, 1996. A Practical Guide to Groundwater and Solute Transport Modeling, John Wiley and Sons, Inc., New York, New York.
- Waterloo Hydrogeologic, 2005. *Visual MODFLOW User's Manual*, Waterloo Hydrogeologic, Waterloo, Ontario.
- URS Corporation, 2001. "Krummrich Groundwater Migration Control Predesign Investigation", Maryland Heights, Missouri, October 4, 2001.
- URS Corporation, 2004. "Remedial Investigation/Feasibility Study Report Sauget Area 2", URS Corporation, St. Louis, Missouri, January 30, 2004.
- URS Corporation, Groundwater Services, Inc., and TRC, 2004. "RCRA Corrective Measures Study (CMS) Solutia Inc. W. G. Krummrich Facility Sauget, Illinois", URS Corporation, St. Louis, Missouri, Groundwater Services, Inc., Houston, Texas, and TRC, August 27, 2004.
- U.S. Army Engineer Division Corps of Engineers, 2005. *Hydrographic Survey Maps Mississippi River, River Mile 200 to Mile 0*, St. Louis District, Missouri.
- Zheng and Bennett, 1995. Applied Contaminant Transport Modeling, Van Nostrand Reinhold, New York, New York.

Part 2: Regional Groundwater Fate and Transport Model

American Bottoms Aquifer



Submitted to:
Mr. Steve Shroff, URS Corp.

April 14, 2008

GSI Environmental Inc.
2211 Norfolk, Suite 1000, Houston, TX 77098

DEVELOPMENT OF A REGIONAL GROUNDWATER FATE AND TRANSPORT MODEL

CONTAMINANT TRANSPORT MODEL EXECUTIVE SUMMARY

Background and Objectives

The southern portion of the American Bottoms aquifer is or has the potential to be affected by constituents originating from several facilities and waste management sites. Although previous modeling efforts have focused on the American Bottoms aquifer, there has been no single integrated flow and fate and transport model that could be used to evaluate all sites of interest on a regional scale.

GSI Environmental Inc. (GSI), formerly known as Groundwater Services, Inc., was retained by URS Corporation to develop a regional groundwater flow and fate and transport model covering a part of the southern portion of the American Bottoms aquifer. This area includes the Sauget Area 1 (SA1) sites, the Sauget Area 2 (SA2) sites, the Krummrich facility (Krummrich), the ConocoPhillips East St. Louis Terminal, and the Clayton Chemical facility.

The objective of this modeling project, as stated in the Groundwater Modeling Plan (GSI, 2006a), was to upgrade/enhance the GSI 2001-2005 groundwater model into a regional model encompassing the Sauget/Cahokia areas such that:

- 1) The modeled flow paths can be validated using actual plume measurements made during the RI phase;
- 2) A sensitivity analysis can be performed to assess how groundwater flow and contaminant nature and extent respond under various remedial alternatives during the FS phase;
- 3) The capture zone of the Sauget Area 2 Groundwater Migration Control System (GMCS) can be further defined; and
- 4) The vertical mass flux of chemicals can be evaluated from both a site-specific and a regional perspective.

In addition, the model can be calibrated to explain constituents at locations identified as locations of concern by the U.S. Environmental Protection Agency (EPA).

Results

The American Bottoms Regional Groundwater Fate and Transport model was developed using data from previous hydrogeologic characterization projects, existing groundwater models, and data developed as part of the SA1 sites, SA2 sites, and Krummrich facility investigations. The MODFLOW groundwater model was then calibrated so that groundwater concentrations simulated in the model were representative of measured groundwater concentrations observed in 2005 and 2006. During calibration, model inputs such as source concentrations, biodegradation rates, dispersion, recharge, pumping rates from certain identified wells, and horizontal hydraulic conductivity were adjusted to reduce the difference between simulated and observed concentration levels. The calibration resulted in a conservative model that may overpredict the impacts of some site constituents.

This section of the report describes the development and calibration of the contaminant transport portion of the model. The development and calibration of the flow portion of the model is described in Part 1 of this report.

Two fate and transport models (MT3D and RT3D) were used to simulate the movement of groundwater plumes from the source zones in the model domain. Simulations started in the 1950 to 1960 time period and were adjusted (calibrated) to match observed groundwater plumes in 2005/2006. The models were then used to forecast plume status up to the year 2038.

The following steps were included in the calibration of the fate and transport model:

- 1) Using the calibrated flow model to account for groundwater flow conditions for the periods of interest;
- 2) Using chlorobenzene as key constituent to develop the model due to the breadth and detailed coverage of the chlorobenzene database;
- 3) Compiling source data to determine size, strength, and temporal patterns in source concentrations;
- 4) Entering source concentration vs. time data in the fate and transport model;
- 5) Building a database of observed concentration data for the calibration period (2005/2006);
- 6) Running the entire model (flow model + fate and transport model) from 1950 to 2003 (period when the GMCS was not active);
- 7) Taking the resulting 2003 plume concentrations and entering these concentrations in a new model for the 2003 to 2005/2006 timeframe (period when the GMCS was active);
- 8) Comparing the modeled concentrations to observed concentrations;
- 9) Changing the model parameters in an attempt to improve the match; and
- 10) Repeating steps 3-9 for other constituents of concern: 1,4-dichlorobenzene (DCB), 2,4-dichlorophenoxyacetic acid (2,4-D), tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (1,2-DCE), and vinyl chloride (VC).

Key results from the calibration efforts for the model are summarized below:

- Historical industrial and highway dewatering activities have had significant effects on the distribution of the observed contaminant plumes today;
- Due to a lack of detailed flow records for industrial and highway dewatering wells, it is impossible to match the current observed plumes precisely. Nevertheless, a model that generally matched the key features of the groundwater plumes was constructed. This model can be used to meet the objectives presented earlier.
- Calibration efforts focused on evaluating the model response to a number of variables, including dispersivity (related to groundwater mixing), biodegradation rates, source decay rates, infiltration, industrial pumping well location and pumping rates, and highway dewatering well flowrates over time. After evaluating these parameters, a "Base Case"

was developed that represented the best match that was achieved by manipulation of model variables.

- Key features of the existing chlorobenzene plume were matched with the model. These features included i) higher concentration zones from the Krummrich, SA1, and SA2 source zones and sources associated with Clayton Chemical; ii) a portion of the Deep Hydrogeologic Unit (DHU) chlorobenzene dissolved plume extending to the northern portion of Site P, north of the main source zone; and iii) the Site R plume and portions of other plumes being captured by the GMCS.
- When all modeled constituents were included, over 94% of the total plume mass flux that would be discharging to the river in 2038 without the GMCS, is predicted to be captured by the GMCS. There is considerable variation in the capture rate for each constituent. For example:
 - Approximately 99% of the total 2,4-D mass flux (~11,000 kilograms per year) is predicted to be captured by the GMCS in 2038.
 - Approximately 91% of the vinyl chloride is predicted to be captured by the GMCS in 2038.
 - Approximately 88% of the chlorobenzene mass flux is predicted to be captured by the GMCS in 2038.
 - Although only 48% of the trichloroethene mass flux is predicted to be captured by the GMCS in 2038, this is a comparatively small plume compared to the mass flux of the other constituents (total mass flux of 17 kilograms per year of TCE going to the river or the GMCS compared to ~21,000 kilograms per year for all seven constituents).

When the highway dewatering system is shut down in 2010, flow from the aquifer to the river will increase, increasing the mass flux to the river. Eventually, however, the mass flux to the river will decrease as the effects of slow source decay overcome the effects of increased river discharge. By the time the system reaches steady state (about 2020), the mass flux to the river will be decreasing steadily and will continue to decrease as the source is depleted.

- Overall, the model presents a conservative estimate of actual conditions present at the site. For example,
 - The model predicts the presence of chlorobenzene in some portions of the Middle Hydrogeologic Unit (MHU) where the actual plume data shows no plume (see Section 5).
 - Based on calibration results, the model uses a lower (slower) biodegradation rate than the Illinois Tiered Approach to Corrective Action Objectives (TACO) (35 IAC 742) standard.
 - Maximum detected concentrations from 1980s to 2006 were used to calculate source concentrations over time for the slow source decay term. For some constituents, this resulted in higher 2006 concentrations than actual measured values.

April 14, 2008



See Section 6.3 for a detailed discussion of the mass flux/capture rate calculations and results.

1.0 INTRODUCTION

As requested by URS Corporation (URS), GSI Environmental Inc. (GSI), formerly known as Groundwater Services, Inc., has developed a regional groundwater fate and transport model of a part of the southern portion of the American Bottoms aquifer.

The development and calibration of the flow portion of the model is described in detail in Part 1 of this report. This section describes the development and calibration of the contaminant transport portion of the model.

2.0 AREA DESCRIPTION

The study area includes the Sauget Area 1 (SA1) sites, the Sauget Area 2 (SA2) sites, the Krummrich facility (Krummrich), the ConocoPhillips East St. Louis Terminal, and the Clayton Chemical facility. Sauget Area 1 is located in Sauget and Cahokia and consists of five former disposal areas (Sites G, H, I, L, and N), one former borrow pit (Site M), and five segments of Dead Creek (CS-B through F) (Roux, 2001). Sauget Area 2 consists of five sites: Sites O, P, Q, R, and S. Site R is a capped area approximately 2000 ft wide (parallel to the Mississippi River) and 500 ft long (perpendicular to the Mississippi River). Groundwater at Site R is currently being controlled by the SA2 Groundwater Migration Control System (GMCS) consisting of a 3300 ft long vertical barrier and three groundwater recovery wells. The Krummrich facility is located entirely in the Village of Sauget. Clayton Chemical is located between Sites O and R. The ConocoPhillips terminal is located east of Site Q-South.

3.0 MODEL OBJECTIVES

The objective of this study, as stated in the Groundwater Modeling Plan (GSI, 2006a), was to upgrade/enhance the GSI 2001-2005 groundwater model into a calibrated regional model such that:

- 1) The modeled flow paths can be validated using actual plume measurements made during the RI phase;
- 2) A sensitivity analysis can be performed to assess how groundwater flow and contaminant nature and extent respond under various remedial alternatives during the FS phase;
- 3) The capture zone of the Sauget Area 2 GMCS can be further defined; and
- 4) The vertical mass flux of chemicals can be evaluated from both a site-specific and a regional perspective.

In addition, the model can be calibrated to explain constituents at locations identified as locations of concern by the U.S. Environmental Protection Agency (EPA).

A numerical groundwater flow and contaminant transport model was developed using the MODFLOW (McDonald and Harbaugh, 1988), MT3D (Waterloo Hydrogeologic, 2006), and RT3D (Clement, 1997) computer codes to meet these objectives.

4.0 CONTAMINANT TRANSPORT MODEL DESCRIPTION

The MT3D mass transport code (Waterloo Hydrogeologic, 2006) was used to evaluate the movement of dissolved chlorobenzene (CB), 1,4-dichlorobenzene (DCB), and 2,4-Dichlorophenoxyacetic acid (2,4-D) migrating in the groundwater. The RT3D mass transport code (Clement, 1997) was used to evaluate the migration and degradation pathways of the dissolved chlorinated solvents tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (1,2-DCE), and vinyl chloride (VC) migrating in the groundwater. Visual MODFLOW Premium Version 4.2 (Waterloo Hydrogeologic Inc.) was used as the pre- and post-processor and as the user interface to the MT3D/RT3D codes.

Key model attributes, assumptions, and input data for the contaminant transport model are listed below.

4.1 Model Capabilities

The model was designed to evaluate the movement of constituent plumes from various source zones in the American Bottoms aquifer and the overlying shallow water-bearing unit. This report summarizes the development of the contaminant transport portion of the groundwater flow and contaminant transport model designed to meet the objectives outlined in Section 3.0.

4.2 Decay Model

MT3D with a first-order biodegradation decay rate for dissolved constituents (i.e., biodegradation of plumes rather than sources) was used to model 1,4-dichlorobenzene, 2,4-D, and chlorobenzene. While the reactive transport model, RT3D, with sequential decay, was used to model the chlorinated solvents PCE, TCE, 1,2-DCE, and vinyl chloride.

4.3 Porosity

An initial effective porosity value of 0.2 was used in the model based on data from the *Focused Feasibility Study Interim Groundwater Remedy Sauget Area 2 Sites O, Q, R, and S* (Solutia, 2002) and the *Source Evaluation Study* (GSI, 2001a). Effective porosity was adjusted during model calibration. Final effective porosities used in the model are discussed in detail in the calibration section (Section 5) of this report.

4.4 Constituents of Concern (COC)

Calibration of the fate and transport model was based on **chlorobenzene** for volatile organic compounds (VOC), **1,4-dichlorobenzene** for semi-volatile organic compounds (SVOC), **2,4-dichlorophenoxyacetic acid** for herbicides, and **tetrachloroethene, trichloroethene, cis-1,2-dichloroethene, and vinyl chloride** for chlorinated solvents.

4.5 Source Assignment

Initial W.G. Krummrich source areas were assigned using DNAPL and sorbed concentration maps from the RCRA Corrective Measures Study. Sauget Area 1 source areas were assigned using DNAPL maps from the DNAPL Characterization and Remediation Study. Clayton source

areas were assigned based on existing groundwater data and source location and strength. Sauget Area 2 source areas were based on existing well concentrations located in Sites O, P, Q, R, and/or S.

The location of source areas was adjusted during model calibration. Final source areas used in the model are discussed in detail in the calibration section (Section 5) of this report.

4.6 Source Concentrations

An Access database was created containing concentration data from 1983 to 2006. Contour data from 2006 URS isoconcentration figures were not used in the database because the contours did not represent lower concentrations needed for model calibration. Coordinates of wells used in the database were obtained from a) boring logs/well construction diagrams, b) URS drawing files, and c) georeferenced scanned figures from various reports and historical documents.

Source concentrations over time in the Shallow, Middle, and Deep Hydrogeologic Units were estimated using data on constituent concentrations at specific wells and at specific times. Concentrations within the three hydrogeologic units were based primarily on results of the Supplemental Investigation.

Supporting constituent concentration data for Sauget Area 1 were obtained from

- a) the *Ecological Risk Assessment for Sauget Area 1* (Menzie-Cura, 2000);
- b) the *Engineering Evaluation/Cost Analysis Remedial Investigation/Feasibility Study* (Roux, 2001);
- c) *RCRA Corrective Measures Study* (URS et al., 2004); and
- d) *Results of DNAPL Characterization and Remediation Study Sauget Area 1*, (GSI, 2005).

Supporting constituent concentration data for Sauget Area 2 were obtained from

- a) Data provided to GSI for development of original groundwater model, 2001;
- b) Data for Roux maps in *Focused Feasibility Study Interim Groundwater Remedy Sauget Area 2, Sites O, Q, R, and S* (Solutia Inc., 2002);
- c) Site P data collected in 2002;
- d) Data provided to GSI for use in Sauget Area 2 *Focused Feasibility Study*, 2003;
- e) GW-1 and GW-2 data provided to GSI by Solutia, 2004;
- f) *Sauget Area 2 Supplemental investigation Phase 2/3* (URS, 2006); and
- g) Concentration data from URS Access Database (URS, 2007).

Supporting constituent concentration data for the Krummrich area were obtained from

- a) *1998 Evaluation of Ground-Water Quality Conditions at the W.G. Krummrich Plant* (Solutia Inc., 1999);
- b) *CA 750 Migration of Contaminated Groundwater Under Control W. G. Krummrich Plant* (URS, 2002);
- c) *Preliminary Results of GW Sampling and Testing at Locations in the vicinity of the W.G. Krummrich Plant* (GSI, 2002);
- d) Data for Roux maps in *Focused Feasibility Study Interim Groundwater Remedy Sauget Area 2, Sites O, Q, R, and S* (Solutia Inc., 2002);
- e) *RCRA Corrective Measures Study* (URS et al., 2004); and

f) *Results of DNAPL Characterization and Remediation Study Sauget Area 1 (GSI, 2005).*

The vertical mass flux of constituents from within the unsaturated zone into the aquifer was incorporated into the model as decaying-concentration source zones in the Shallow Hydrogeologic Unit (SHU) (Layer 1).

Initially, source concentrations were assumed to be equal to observed average concentrations within a source zone. Historical and future source concentrations were estimated by projecting source concentrations backward and forward in time assuming a conservative first-order source decay half-life of 40 years (Section 4.9). Projected historical source concentrations did not exceed the water solubility of any of the groundwater constituents. Source concentrations were adjusted during model calibration. Final source concentrations used in the model are discussed in detail in the calibration section (Section 5) of this report.

A number of samples for chlorinated ethenes had relatively high values (e.g., well GM-33 at <10,000 ug/L PCE); however, these samples were non-detect values with high detection limits due to the presence of high concentrations of other organics. Due to the nature of this information (non-detect, but with a very wide range of possible values) these data were not used for this modeling study.

4.7 Initial Concentrations

Sources at the site began potentially in the 1920s. Assuming a general travel time of 10-30 years from distance sources to discharge points, a model start time of 1950 was selected as a conservative value. Therefore, to establish representative starting concentrations, MT3D/RT3D was run for approximately 46 years, and the resulting concentrations were then compared to concentrations observed in monitoring wells at the site in 2006. During the calibration process, using a starting time of 1960 (Section 5.1) instead of 1950 decreased the model run time without a significant impact to the calibration statistics, therefore all runs after the initial calibration runs had a simulation start time of 1960.

Since Visual Modflow does not permit a barrier wall to turn on and off, the initial simulation was run in two segments. The first segment was from 1960 to 2003 and did not include the GMCS. Concentrations from this segment were then used as starting concentrations for the next segment. The second segment was from 2003 to 2006 and included the GMCS.

Source locations and strengths for this initial period were adjusted until the concentrations predicted by the MT3D/RT3D model were within reasonable agreement with observed concentrations. This 46-year concentration distribution was then used as the initial condition for all subsequent mass transport modeling.

4.8 Biodegradation and Sorption

Biodegradation kinetics of all dissolved constituents (i.e., groundwater plumes) were assumed to be first-order. Initial dissolved-phase biodegradation rates for each COC were obtained from Illinois Tiered Approach to Corrective Action Objectives (TACO) (35 IAC 742) standard. These rates for chlorobenzene were adjusted during calibration so that the predicted concentrations were in reasonable agreement with observed concentrations at the site. The adjusted

biodegradation rates used in the model are conservative relative to TACO rates as discussed in detail in the calibration section (Section 5) of this report.

Adsorption of organic species and arsenic was assumed to be linear. Retardation factors for simulating sorption of dissolved constituents to aquifer media were calculated from distribution coefficients calculated using K_{oc} taken from the TACO standard (35 IAC 742) and assuming a fraction organic carbon (f_{oc}) of 0.0016 (URS, 2004). The following soil-water distribution coefficients (K_d) were initially used in the model:

Constituent	K_d (L/kg)
Chlorobenzene	3.5×10^{-1}
1,4-Dichlorobenzene	9.9×10^{-1}
2,4- Dichlorophenoxyacetic acid	7.2×10^{-1}
Tetrachloroethene	2.5×10^{-1}
Trichloroethene	2.7×10^{-1}
cis-1,2-Dichloroethene	5.7×10^{-2}
Vinyl chloride	3.0×10^{-2}

4.9 Source Decay

The source decay coefficient represents how quickly the source is being depleted and can be derived using estimates of the source mass and the rate at which contaminants leave the source (Newell et al., 1996). Based on median values calculated for the MHU and DHU in the *Sauget Area 2 Focused Feasibility Study* (GSI, 2003a) and *Source Evaluation Study* (GSI, 2001), a conservative first-order source decay half-life of 40 years was used in the model initially. Although source decay half-lives were calculated for Krummrich in *Time to Clean Estimates* (GSI, 2004), these values were based on a uniform 11 ft source thickness rather than the entire source and, therefore, were not used in the fate and transport model.

Note that this approach for modeling the source strength vs. time *does not* mean that all the sources in the model were assumed to be attenuated within 40 years. Rather, this approach assumed the sources were decaying relatively slowly, with the source concentration falling by 50% every 40 years. Because most of the source zones had high starting concentrations relative to the groundwater protection standards, all these sources persisted in the model for more than 40 years.

Source decay half-lives were adjusted during model calibration. Final source decay half-lives used in the model are discussed in detail in the calibration section (Section 5) of this report.

4.10 Dispersion

Dispersion refers to the process by which a plume spreads out longitudinally (along the direction of groundwater flow), transversely (perpendicular to groundwater flow), and vertically due to mechanical mixing and molecular diffusion. Initially, a longitudinal dispersivity value of 32 ft was

used in the model based on the Xu and Eckstein (1995) equation. A transverse/longitudinal dispersivity ratio of 0.1 and a vertical/longitudinal dispersivity ratio of 0.01 were used in the model (Aziz et. al. 2000). Longitudinal dispersion was varied during calibration. Final dispersion values used in the model are discussed in detail in the calibration section (Section 5) of this report.

4.11 Concentration Observation Wells

Concentration observation wells for each COC were imported into the model at locations where concentrations were measured during the 2005-2006 Supplemental Investigation for comparison of simulated to measured concentrations. The midpoint of the screen interval was used as the measurement point depth for the concentration in the observation wells. For some constituents (such as the chlorinated ethenes), the observed plumes were relatively small and had only a few wells with detectable values. For example, the TCE plume in the SHU only had four wells with detectable values, although other wells were non-detect within non-detect limits (i.e., "< 10,000 ug/L"). The calibration process used the data with reliable information (the wells with detectable values, and non-detect wells with low detection limits) to produce a simulated plume that matched the actual plume.

4.12 Hydraulic Conductivity

Although varying the horizontal hydraulic conductivity was evaluated during the calibration of the contaminant transport model, it did not result in an improved calibration. Therefore, the horizontal and vertical hydraulic conductivities in the final model remained unchanged from the flow model.

5.0 MODEL CALIBRATION

Calibration is the process of adjusting model parameters until the difference between modeled outputs and site-specific data are reduced to an acceptable level.

Both qualitative and quantitative comparisons were made between the model and site-specific information. Qualitative flow comparisons included comparison of observed spatial plume distribution to the spatial distribution of the simulated plumes. Quantitative flow model comparisons included the comparison of simulated concentrations to measured concentrations and a comparison of the sum of the residual differences between the two.

Concentration data collected during the 2005-2006 Supplemental Investigation were used for a more detailed calibration in the Site area.

Over 320 simulations were run during the contaminant transport calibration process using various combinations of input parameters. The model was calibrated in the sequence described in the following sections.

5.1 Initial Qualitative Model Comparison

Qualitative Calibration Case 1

Initially, the model was run from 1950 to 2006 using a dispersivity of 32 ft and no biodegradation or retardation, and with the GMCS barrier wall in place throughout the simulation, but the GMCS pumping wells turning on in December 2004. The constituent used for calibration was chlorobenzene. Based on historical potentiometric surface maps, the River Ranney-type well was placed approximately 3000 ft north of Site R. The Plant Ranney-type wells were placed north of the W.G. Krummrich employee parking lot. Calibration runs based on these initial model assumptions indicated that the predicted chlorobenzene concentrations in the MHU and DHU were considerably higher than the measured values (Figures 2 and 3).

Qualitative Calibration Case 2

Based on personal communication with Solutia Inc, the River Ranney-type well was moved to a location 600 ft north of Site R. The North Plant Ranney-type well was relocated to the northwestern tip of the parking lot while the South Ranney-type well was relocated inside the plant. The model was then run with no retardation and no biodegradation. Although a qualitative improvement in chlorobenzene concentrations was observed (Figures 4 and 5), the concentrations in the MHU and DHU were still higher than measured values.

Note that these initial placements of the Ranney wells in the earliest versions of the transport model were incorrect. Research performed by the Sauget Area 2 companies yielded historic plant documents that revealed the actual locations of these wells (see Qualitative Calibration Case 7 below).

Qualitative Calibration Case 3

Since Visual Modflow does not permit a barrier wall to be activated in the middle of a simulation, the simulations were then divided into two segments: one from 1950 to 2003 with no GMCS and the other from 2003 to 2006 with the GMCS in place. Although the chlorobenzene concentrations predicted by the no GMCS segment were qualitatively similar to those of simulations in which the slurry wall was active throughout (Figures 6 and 7), all subsequent models were run in the two segments mentioned above.

Qualitative Calibration Case 4

After dividing the simulations into two segments, the model was run with a chlorobenzene retardation factor of 6 and a first-order biodegradation rate constant of 0.0023 day^{-1} (based on the Illinois TACO reported half life of 301 days for chlorobenzene). These simulations predicted significantly smaller chlorobenzene plumes (Figures 8 and 9).

Qualitative Calibration Case 5

Although limited improvement in the chlorobenzene plume length was observed by running the model with retardation only (no biodegradation) (Figures 10 and 11), qualitatively, the overall footprint of the chlorobenzene plume was still significantly different from the measured plume with no simulated chlorobenzene near the northern portion of the DHU in Site P.

Qualitative Calibration Case 6

Decreasing the retardation factor by half (to $R=3$) resulted in a larger plume, but with significantly higher chlorobenzene concentrations than those in the measured plume (Figures

12 and 13). However, the reduced retardation factor expanded the plume into the northern DHU portion of Site P, an important qualitative calibration goal established by the EPA to explain constituents found in well OSAA-1.

Qualitative Calibration Case 7

Chlorobenzene concentration data from other sources were then added to the model, and all source concentrations were set to the maximum observed value at each source rather than the average observed value. Based on historical Monsanto documents (Ecology and Environment, 1988; Midwest Rubber, 1969, and Monsanto, date unknown_a,b), the River Ranney-type well was relocated to the northeast tip of Site R and the Plant Ranney-type wells were moved to the locations shown in Figure 14.

After a trial and error process, using a dispersivity of 46 ft, retardation factor of 1.0, a chlorobenzene biodegradation rate constant of 0.0011 day^{-1} ($t_{1/2} = 602 \text{ days}$), and increasing the infiltration rate to 7.645 in/yr yielded a more favorable correlation of simulated and measured chlorobenzene values (Figures 15 and 16). These parameters were then used as the initial values for the subsequent quantitative calibration. Initiating the model run in 1960 instead of 1950 decreased the model run time, but did not indicate any significant differences, so the starting year of 1960 was also retained for subsequent calibration runs.

5.2 Quantitative Calibration

Initial quantitative calibration of the transport model was based on chlorobenzene because chlorobenzene concentrations comprised the most complete set of observed values. Once the overall modeling parameters were calibrated, the model was calibrated to each of the other COC specific parameters.

5.3 Base Case Model – Calibration Results

Initial quantitative calibration of the transport model yielded an overall RMS error of 7.64 mg/L with a mean residual error of 0.53 mg/L.

Statistic	Site Area		
	Overall	MHU	DHU
RMS Error(mg/L)	7.64	9.14	5.21
MR Error (mg/L)	0.53	1.34	-0.47

Initial calibration runs indicated that the predicted concentrations from both the MHU and DHU were higher than the measured values. Therefore, base case parameters were adjusted to produce a better match between measured and simulated chlorobenzene concentrations.

5.3.1 Biodegradation Rate Constant Study

Varying the chlorobenzene first-order biodegradation rate constant did not improve the difference between the measured and calculated concentrations. Decreasing the rate constant by a factor of four ($t_{1/2} = 1204$ days) yielded an overall RMS error of 7.6 mg/L and an MR error of 1.4 mg/L. Although an improvement in the RMS error was observed, the MR errors increased, indicating an overall overprediction of concentrations in the model by decreasing the biodegradation rate.

Statistic	Site Area		
	Overall	MHU	DHU
RMS Error (mg/L)			
Base Case	7.64	9.14	5.21
Rate Const Study	7.61	9.25	4.84
MR Error (mg/L)			
Base Case	0.53	1.34	-0.47
Rate Const Study	1.37	2.16	0.39

As seen in the table, adjustment of the chlorobenzene half-life did not improve the model calibration, so the base model chlorobenzene half-life was retained.

As an additional check on the validity of the degradation rates, the mass flux of chloride and the chloride generation rate vs. distance were analyzed. Although there is considerable variation in the chloride data, these analyses indicate that the biodegradation rates used in the model are plausible and are not contradicted by the chloride dataset.

To calculate the **mass flux** of chloride, a vertical cross section was drawn between SA2-MW-5-(unit) and SA2-MW-1-(unit) wells comprised of the following wells:

Well	Chloride Concentration (mg/L)	
	MHU	DHU
SA2-MW-5-M, SA2-MW-5-D	51	25
SA2-MW-4-M, SA2-MW-4-D	140	78
GM-60B (Middle), PSMW-12 (Deep)	160	70
SA2-MW-2-M, SA2-MW-2-D	150	300
SA2-MW-1-M, SA2-MW-1-D	180	270
AVERAGE	136	150
Approximate Background Cl ⁻ Conc.*	25	25
"EXCESS" CHLORIDE**	111	125

* (from IMW-1D and IMW-1S; Schicht 1965)

** Excess Chloride = Average - Background

Next, the flow across this cross section was estimated by using flow data from the GMCS (450 gpm captures approximately 2,100 ft of aquifer cross section) and the width of the chloride mass flux cross section (5,650 ft). With this approach a flow of 2.4×10^9 liters per year was estimated, or approximately 1.2×10^9 liters per year in the MHU and DHU, respectively.

Mass flux in units of kilograms per year of chloride was then calculated by taking the flowrate times the excess chloride concentration in the cross section (the average was used because the five wells were equally spaced). The source loading of chlorobenzene from the two most important source zones (the Krummrich chlorobenzene process unit and Site I) was also estimated. Both the chloride mass flux and the mass flux of chlorobenzene being emitted by the source zones were converted to units of kilomoles per year to make a stoichiometric comparison of the relative mass flux terms. This calculation yielded the following results:

Row	Variable	Site Area		
		Units	MHU	DHU
1	Excess Chloride Concentration in Cross-Section	mg/L	111	125
2	Flowrate through Cross-Section in Each Unit	Liters/yr	1.2×10^9	1.2×10^9
3	Chloride Mass Flux through X-Section in Each Unit	kg/yr	133,000	150,000
4	Chloride Mass Flux through X-Section in Each Unit*	kmoles/yr*	3800	4300
5	Mass of chlorobenzene emitted by Krummrich CB process unit and Site I sources (two largest source zones upgradient of X-sect) (see box next page)	kg/yr	~53,000	~9,000
6	Mass of chloride produced from chlorobenzene biodegradation, assuming 100% of chlorobenzene biodegrades**	kmoles/yr**	470	80
7	Is there enough chloride in aquifer to account for chlorobenzene biodegradation, even assuming 100% is biodegraded? (Is row 4 greater than row 6?)	-	YES	YES

* (using 35 kilomoles per kilogram for chloride)

** (using 113 kilograms per kilomole for chlorobenzene)

In conclusion, there is enough chloride in the aquifer to account for biodegradation of chlorobenzene as simulated in the model. Note that this analysis did not account for dichlorobenzene or other chlorinated species. However, the chloride contribution from the other chlorinated compounds is likely to be much smaller than chlorobenzene because the other constituents have much lower source concentrations than chlorobenzene (for example, the average of the MHU/DHU chlorobenzene concentrations for the Krummrich chlorobenzene process unit and Site I is 104 mg/L in 2006, compared to 19 mg/L for dichlorobenzene at the same locations in 2006). Because there is so much excess chloride (8100 total kilomoles per year for chloride in the MHU + DHU compared to only 830 kilomoles per year of chlorobenzene being emitted from their source zones), addition of the other chlorinated compounds would not likely change the conclusions. Other sources of chloride, which might explain the difference between moles of excess chloride and models of chlorobenzene, include discharge from a

source of chloride on the surface (e.g., salt piles) or as an artifact of data scatter (due to the extreme mixing of the plume due to dewatering and industrial pumping).

A simple evaluation of **chloride vs. distance** was also performed using three well pairs in and downgradient of the Krummrich chlorobenzene process unit. While there is considerable scatter in these data, there does appear to be a possible trend of increasing chloride concentrations downgradient of this source zone, as shown by the table showing concentration vs. distance wells:

**SOURCE CONCENTRATION CALCULATIONS FOR CHLORIDE/CHLOROBENZENE
MASS FLUX ANALYSIS**

From MHU Sources Figure (Figure 25):

Krummrich chlorobenzene process unit (green source area) CB concentration in 2003: 308 mg/L. Site I (grey source area) CB concentration in 2003: 49 mg/L. (other source areas and COCs small compared to these two). Averaging these two values yields **179 mg/L** as the chlorobenzene source concentration in the model for these two major source zones upgradient of the cross section.

From DHU Sources Figure (Figure 26):

Krummrich chlorobenzene process unit (blue source area) CB concentration in 2003: 49 mg/L. Site I (brown source area) CB concentration in 2003: 10 mg/L. Averaging these two values yields **30 mg/L** as the chlorobenzene source concentration in the model for these two major source zones upgradient of the cross section.

Each source zone width parallel to groundwater flow is approximately 720 ft wide, or about a third the GMCS width. Therefore, for two source zones @ 720 ft/source zone, the total flow would be approximately two thirds the GMCS flowrate, or 300 gpm (5.99×10^8 liters per year). This is equal to 2.98×10^8 liters per year flowing through the major chlorobenzene source zones in each of the MHU and DHU units.

Multiplying the average source concentrations by the 5.99×10^8 liters per year flowrate gives 53,000 kilograms chlorobenzene being emitted per year in the MHU and 9,000 kilograms per year in the DHU.

Concentration vs. Distance Wells	Chloride Concentration (mg/L)	
	MHU	DHU
GM-9B and GM-9C (in Krummrich chlorobenzene process unit)	82	16
PSMW-8, MW-7C (in Lot F)	110	110
SA2-MW-4-M, SA2-MW-4-D (Upgradient of Site R)	140	78
"EXCESS" CHLORIDE (source minus upgradient of Site R)	58	62

By averaging the potential increase in concentration, 60 mg/L of chloride was either generated by biodegradation of chlorinated compounds (or by discharge from a source of chloride on the surface (i.e., salt piles)) or as an artifact of data scatter. However, the 60 mg/L of increase is equivalent to 1.7 millimoles chloride per liter, or a potential 194 mg/L of chlorobenzene (based on a stoichiometric analysis and assuming 100% biodegradation). Since the average concentration of the Krummrich chlorobenzene process unit/Site I MHU and DHU source zones is only 104 mg/L, there appears to be more than enough excess chloride present to explain the modeled biodegradation at the site based on data from these wells. Note that selection of other wells could result in alternative results due to the scatter in the data, and therefore this analysis is probably less reliable than the preceding mass flux calculation. However, this analysis does show that the biodegradation rates used in the model are consistent with this particular chloride concentration vs. distance analysis.

5.3.2 Source Decay Life Time Study

Decreasing the source decay half-life from 40 yrs to 20 yrs improved the overall RMS error but increased the overall MR error, indicating an overall increase in the under prediction by the model than the base case.

Statistic	Site Area		
	Overall	MHU	DHU
RMS Error (mg/L)			
Base Case	7.64	9.14	5.21
Source Decay Study	5.93	5.50	6.42
MR Error (mg/L)			
Base Case	0.53	1.34	-0.47
Source Decay Study	-1.38	-0.53	-2.44

Because no significant improvement to the base case was observed with adjustment of the source decay half-life, the base model source decay half-life of 40 years was retained.

5.3.3 Reactive Transport Study (RT3D vs. MT3D)

Employing the RT3D model with instantaneous aerobic decay and a starting oxygen concentration of 6 mg/L and an O₂:Cl ratio of 2.0 resulted in an overall RMS error of 9.4 mg/L and a MR error of 4.6 mg/L. Additionally, the model required a run time greater than 12 hours. Decreasing the oxygen concentration to 2 mg/L and running the model from 1978 to 2003 to decrease run time resulted in an overall RMS error of 8.2 mg/L and a residual mean error of 2.8 mg/L.

Statistic	Site Area		
	Overall	MHU	DHU
RMS Error (mg/L)			
Base Case	7.64	9.14	5.21
RT3D Study (6 mg/L O ₂)	9.41	10.27	8.21
RT3D Study (2 mg/L O ₂)	8.24	9.37	6.47
MR Error (mg/L)			
Base Case	0.53	1.34	-0.47
RT3D Study (6 mg/L O ₂)	4.59	4.54	4.65
RT3D Study (2 mg/L O ₂)	2.83	2.74	2.95

Because no significant improvement to the base case was observed with the use of instantaneous reaction kinetics instead of first-order kinetics, the base model source decay half-life was retained.

An attempt was made to run the model using RT3D with an oxygen starting concentration of 2 mg/L and an O₂:Cl ratio of 2.0. However, this simulation was abandoned because of insufficient progress after running for 24 hours (i.e., the model would have taken too long to run to be of practical interest for this project).

5.3.4 Vertical Gradient Study (Flow model)

To study vertical gradient effects in the model, the horizontal hydraulic conductivity of the DHU was increased by 20%, the model run for 2 months, and changes in the potentiometric surface were then observed. This study was performed in an attempt to reproduce the observed pattern of chlorobenzene in the DHU near the northern portion of Site P but not in the MHU. The calibrated flow model (recharge = 7.6 in/yr) was used in this study. Although the vertical gradient study showed a slightly better overall RMS error, the individual RMS errors and MR error in the MHU and DHU indicated the base case flow model resulted in a better calibration, so the base case hydraulic conductivity was retained.

Statistic	Site Area			
	Overall	SHU	MHU	DHU
RMS Error (ft)				
Flow Model	0.70	0.78	0.60	0.64
Vertical Gradient Study	0.69	0.75	0.63	0.66
MR Error (ft)				
Base Case	0.005	0.09	-0.05	-0.11
Vertical Gradient Study	-0.09	-0.03	-0.12	-0.20

5.3.5 North Plant Pumping Study

The effect of the Plant Ranney-type wells on contaminant transport were studied by dividing the total flow rate equally between the two north wells (Figure 14) and turning off the other three wells. This adjustment did not result in significant improvement of the model calibration, so the original base case scenario was retained.

Statistic	Site Area		
	Overall	MHU	DHU
RMS Error (mg/L)			
Base Case	7.64	9.14	5.21
North Plant Study (no wells on)	7.62	8.98	5.48
North Plant Study (2 wells)	7.67	8.98	5.50
MR Error (mg/L)			
Base Case	0.53	1.34	-0.47
North Plant Study (no wells on)	0.44	1.23	-0.58
North Plant Study (2 wells)	0.42	1.2	-0.60

5.3.6 Transient Recharge and Mississippi River Stage Study

Next, an annual average river stage and infiltration rate for each year of pumping data available were incorporated into the model. This model required a run time of approximately 12 hours compared to about 4 hours for the base case, and the overall RMS error did not show a significant improvement.

Statistic	Site Area		
	Overall	MHU	DHU
RMS (mg/L)			
Base Case	7.64	9.14	5.21
Transient Study (MT3D)	7.66	8.96	5.52
Mean Residual (mg/L)			
Base Case	0.53	1.34	-0.47
Transient Study (MT3D)	0.28	0.99	-0.65

5.3.7 Historical Industrial Wells Study

During the course of the calibration, the impact of historical pumping on contaminant transport was discovered to be of great significance (see Section 7.4 of Part 1). Historical pumping data from 1960 to 1985 (Schicht, et al., 1984a-b; Ritchey et al., 1984a-c), 1990 (Schicht and Buck, 1995), and 1994 (Olson and Sanderson, 2000) were obtained. Based on the Illinois State

Water Survey Division historical groundwater model (Schicht et al., 1984a-b; Ritchey et al., 1984c-e), seven additional historical industrial wells lying in the model domain were added to the model (Figure 14) to represent regional industrial wells. Based on the information obtained (Ritchey et al., 1984e), these industrial wells phased out of production after 1981.

No significant improvement in the RMS or MR errors were observed, and because this model required a longer running time than the base case, the base case model was retained.

Statistic	Site Area		
	Overall	MHU	DHU
RMS (mg/L)			
Base Case	7.64	9.14	5.21
Well Study	7.72	8.48	5.72
Mean Residual (mg/L)			
Base Case	0.53	1.34	-0.47
Well Study	0.53	1.15	-0.82

5.4 Final Calibration

For the final calibration of the contaminant transport model, the base case was used as a starting point and various combinations of highway dewatering pumping rates, infiltration rate, effective porosity, source concentration, source area, and biodegradation rates were manually changed until a better agreement between the simulated and measured concentrations was achieved.

Highway Dewatering Well Pumping Rates

Because pumping rate information for highway dewatering wells was unavailable after 1994, these flow rates were adjusted during calibration. Total pumping rates incorporated in the model ranged from 6250 to 7628 gpm. Better agreement between simulated and measured concentrations was achieved by increasing the 2003 to 2010 total interstate pumping rate from 6250 gpm to 6828 gpm (Table 1).

Infiltration Rate

Increasing the infiltration rate from 7.6 in/yr to 7.8 in/yr improved the agreement between simulated and measured concentrations.

Porosity

Although effective porosities ranging from 0.2 to 0.33 for the SHU and 0.1 to 0.24 for the MHU and DHU were applied to the model, better agreement between simulated and measured concentrations was achieved by using an effective porosity of 0.3 for the SHU and 0.18 for the MHU and DHU.

Chemical Specific Parameters

Biodegradation Rate Constant

Dissolved-phase biodegradation rates from Illinois TACO standard were used for all constituents except for the chlorobenzene rates for the MHU, and PCE, TCE, and 1,2-DCE. A better match to actual data was obtained by reducing the chlorobenzene biodegradation rates in the MHU by 50%, and reducing the PCE, TCE, and 1,2-DCE rates by 50%, 62%, and 25%, respectively. Final biodegradation half-lives used in the model were:

Constituent	TACO Half-Life (days)	Modeled Half-Life (days)
Chlorobenzene (SHU)	301	301
Chlorobenzene (MHU)	301	462
Chlorobenzene (DHU)	301	301
1,4-Dichlorobenzene	365	365
2,4- Dichlorophenoxyacetic acid	180	180
Tetrachloroethene	722	361
Trichloroethene	1650	630
cis-1,2-Dichloroethene	2888	2166
Vinyl chloride	2888	2166

Based on these half-lives, the individual rates (biodegradation rate = $\ln(2)/\text{half-life}$) used in the calibrated model are presented below:

Constituent	Biodegradation Rate Constant (day ⁻¹)		
	SHU	MHU	DHU
1,4-Dichlorobenzene	0.0019	0.0019	0.0019
2,4-Dichlorophenoxyacetic acid	0.0038	0.0038	0.0038
Chlorobenzene	0.0023	0.0015	0.0023

The RT3D model was used for modeling the sequential decay of the chlorinated solvents. The decay rates for each COC were adjusted individually until the best possible agreement between simulated and measured concentrations was achieved. The individual rates used in the calibrated model are presented below:

Constituent	Biodegradation Rate Constant (day ⁻¹)		
	SHU	MHU	DHU
Tetrachloroethene	0.0019	0.0019	0.0019
Trichloroethene	0.0011	0.0011	0.0011
cis-1,2-dichloroethene	0.0003	0.0003	0.0003
Vinyl chloride	0.0003	0.0003	0.0003

Source Area

Source areas for each COC were adjusted individually until the best possible agreement between simulated and measured concentrations was achieved. The individual concentrations used in the calibrated model are shown on Figures 17 through 27.

Source Concentration

As discussed above, source size and concentration were used as a calibration parameter. For this purpose, source concentrations for each COC were adjusted individually until the best possible agreement between simulated and measured concentrations was achieved. The individual concentrations used in the calibrated model are shown on Figures 17 through 27.

For chlorobenzene, most of the concentrations at Site R were considerably higher in the 1980s than in the 2000s. Therefore, Site R calibration focused on matching these 1980s concentrations in wells GM-27, GM-28B, B29-B, and B-27B in MHU and GM-57C and GM-28C in DHU (Table 2).

5.5 Mass Flux

One project objective was to determine the percent of dissolved constituent mass flux¹ captured by the GMCS. For this calculation, the quantity of groundwater flowing into the river and the concentration of dissolved constituents in the groundwater discharged to the river were needed. These quantities were calculated using the ZoneBudget feature of MODFLOW in conjunction with mass transport simulations using MT3D/RT3D.

ZoneBudget is a water balance component within Visual MODFLOW that calculates the exchange of groundwater between adjacent user-established zones. The calculation accounts for inflow into a zone from all sources, and outflow through model edges and internal sinks. To calculate the transfer of water from the area under the site to the river, numerous separate zones were defined representing the aquifer adjacent to the river and the river itself (Figures 28 to 30). Separate river and aquifer zones were established for each horizon since initial constituent concentration differed between layers. The quantity of water flowing from each layer into the river zone was calculated by ZoneBudget and the sum was used as water flow to the river.

Each horizon near the site was divided into 12 zones (Figures 28 to 30). The mass lost to the river was calculated by the following procedure:

1. MODFLOW, ZoneBudget and MT3D/RT3D were run: a) without the GMCS and then, b) with the GMCS. Then, for each case, the rate of groundwater discharge to the river from each aquifer zone reported by ZoneBudget was used in the mass balance calculations.
2. The concentration in each aquifer zone that discharged to the river was estimated by placing a concentration observation well in each horizon zone. This concentration represented the dissolved constituent concentration discharged to the river from each zone. The

¹ Mass flux is the mass per time (kilograms per year) that crosses a certain vertical control plane in an aquifer. In this case the vertical plane extends from the surface to bedrock on a line adjacent to the Mississippi River.

concentrations were recorded by MT3D/RT3D at periodic intervals for use in the mass balance calculations.

3. The total mass discharged to the river after a particular modeling period was calculated as the sum of the products of the river discharge and concentrations in each zone as follows:

$$M_R = \sum_{i=1}^{\text{number of zones}} Q_i C_i$$

where Q_i = discharge rate of groundwater from zone i into the river
 C_i = final constituent concentration in zone i
 M_R = mass discharged to river

6.0 FINAL MODEL CALIBRATION RESULTS

6.1 Quality of Fit Between Actual and Predicted Concentrations

Because of a lack of detailed flow records for industrial and highway dewatering wells, it is impossible to match the current observed plumes precisely. However, overall, the mass transport model generally matches the key features of the groundwater plumes as described below.

A number of samples for chlorinated ethenes had relatively high values (e.g., well GM-33 at <10,000 ug/L PCE); however, these samples were non-detect values with high detection limits due to the presence of high concentrations of other organics. Because these values were non-detectable for the chlorinated ethenes and due to the nature of this information (non-detect, but with a very wide range of possible values) these data were not used for this modeling study.

Chlorobenzene

The modeled chlorobenzene plume extends north to an area near the northern portion of Site P, an important qualitative calibration goal expressed by the EPA. Because of uncertainties in historical industrial pumping, the exact plume configuration was not matched (the simulated northern lobe is too far to the east), but the calibration goal (a northern lobe of the chlorobenzene plume) was captured by the model. RMS errors for the shallow, middle, and deep hydrogeologic layers were 4.7, 4.7, and 2.3 mg/L, respectively, with an overall RMS of 4.2 mg/L for all layers combined. MR errors of 0.9, 0.4, and -0.1 mg/L were obtained, respectively, for the SHU, MHU, and DHU, and 0.5 mg/L for all layers combined. Chlorobenzene calibrated plumes are shown on Figures 28 through 38, while Figures 39 through 41 show the spatial correlations between the measured and simulated groundwater concentrations.

Statistic	Site Area			
	Overall	SHU	MHU	DHU
RMS (mg/L)	4.19	4.71	4.66	2.28
Mean Residual (mg/L)	0.48	0.88	0.43	-0.11

Note that the differences between the modeled and actual plume configuration are the result of very sharp boundaries in the observed plume geometry. For instance, in the MHU, the model is unable to reproduce very low concentrations at GM-3 (0.54 ug/L measured) while at the same time reproduce concentrations 60,000 times greater at MW-3B (39,000 ug/L measured) less than 1000 ft south of GM-3. Removing wells GM-3 and MW-3B from the calibration results in the MHU and DHU combined RMS error decreasing from 3.78 mg/L to 2.42 mg/L. Similarly, in the DHU, removing low concentration wells PSMW-7 (320 ug/L measured) and MW-3C (480 ug/L measured) ~1400 ft west of a concentration location ~70,000 times greater (GM-4B, 22,000 ug/L measured) further decreases the RMS error to 2.22 mg/L.

The modeled chlorobenzene plume is likely to be conservative in that it overestimates the northern extent of the chlorobenzene plume in the MHU. While chlorobenzene has been observed in the DHU near the northern portion of Site P, there is no detectable chlorobenzene in the MHU in this area. Attempts to reproduce the observed pattern were unsuccessful, and the current model overestimates the extent of the MHU chlorobenzene plume in the northern portion of the study area.

1,4-Dichlorobenzene

1,4-Dichlorobenzene calibrated plumes are shown on Figures 42 through 49, while Figures 50 through 52 show the spatial correlations between the measured and simulated groundwater concentrations. RMS errors for the shallow, middle, and deep hydrogeologic layers were 0.8, 0.4, and 0.6 mg/L, respectively, with an overall RMS of 0.6 mg/L for all layers combined. MR errors of 0.1, 0.1, and 0.2 mg/L were obtained, respectively, for the SHU, MHU, and DHU, and 0.1 mg/L for all layers combined.

Statistic	Site Area			
	Overall	SHU	MHU	DHU
RMS (mg/L)	0.62	0.78	0.45	0.56
Mean Residual (mg/L)	0.15	0.14	0.14	0.19

2,4-Dichlorophenoxyacetic acid

2,4-Dichlorophenoxyacetic acid calibrated plumes are shown on Figures 53 through 60, while Figures 61 through 63 show the spatial correlations between the measured and simulated groundwater concentrations. RMS errors for the shallow, middle, and deep hydrogeologic layers were 4.4, 0.9, and 0.4 mg/L, respectively, with an overall RMS of 2.8 mg/L for all layers combined. MR errors of -0.6, -0.1, and 0.1 mg/L were obtained, respectively, for the SHU, MHU, and DHU, and -0.2 mg/L for all layers combined.

Statistic	Site Area			
	Overall	SHU	MHU	DHU
RMS (mg/L)	2.81	4.41	0.89	0.42
Mean Residual (mg/L)	-0.24	-0.58	-0.07	0.07

Tetrachloroethene

Tetrachloroethene calibrated plumes are shown on Figures 64 through 69, while Figures 70 through 72 show the spatial correlations between the measured and simulated groundwater concentrations. RMS errors for the shallow, middle, and deep hydrogeologic layers were 0.01,

0.004, and 0.002 mg/L, respectively, with an overall RMS of 0.01 mg/L for all layers combined. MR errors of -0.002, 0, and -0.001 mg/L were obtained, respectively, for the SHU, MHU, and DHU, and -0.001 mg/L for all layers combined.

Statistic	Site Area			
	Overall	SHU	MHU	DHU
RMS (mg/L)	0.01	0.01	0.004	0.002
Mean Residual (mg/L)	-0.001	-0.002	0.0	-0.001

Trichloroethene

Trichloroethene calibrated plumes are shown on Figures 73 through 78, while Figures 79 through 81 show the spatial correlations between the measured and simulated groundwater concentrations. RMS errors for the shallow, middle, and deep hydrogeologic layers were 0.03, 0.01, and 0.004 mg/L, respectively, with an overall RMS of 0.02 mg/L for all layers combined. MR errors of -0.003, 0, and 0 mg/L were obtained, respectively, for the SHU, MHU, and DHU, and -0.001 mg/L for all layers combined.

Statistic	Site Area			
	Overall	SHU	MHU	DHU
RMS (mg/L)	0.02	0.03	0.01	0.004
Mean Residual (mg/L)	-0.001	-0.003	0.0	0.0

cis-1,2-Dichloroethene

cis-1,2-dichloroethene calibrated plumes are shown on Figures 82 through 89, while Figures 90 through 92 show the spatial correlations between the measured and simulated groundwater concentrations. RMS errors for the shallow, middle, and deep hydrogeologic layers were 0.02, 0.08, and 0.05 mg/L, respectively, with an overall RMS of 0.06 mg/L for all layers combined. MR errors of 0.006, 0.02, and 0.01 mg/L were obtained, respectively, for the SHU, MHU, and DHU, and 0.01 mg/L for all layers combined.

Statistic	Site Area			
	Overall	SHU	MHU	DHU
RMS (mg/L)	0.06	0.02	0.08	0.05
Mean Residual (mg/L)	0.01	0.006	0.02	0.01

Vinyl chloride

Vinyl chloride calibrated plumes are shown on Figures 93 through 100, while Figures 101 through 103 show the spatial correlations between the measured and simulated groundwater concentrations. RMS errors for the shallow, middle, and deep hydrogeologic layers were 0.04, 0.04, and 0.08 mg/L, respectively, with an overall RMS of 0.05 mg/L for all layers combined. Mean residual errors of 0.02, 0.03, and 0.04 mg/L were obtained, respectively, for the SHU, MHU, and DHU, and 0.03 mg/L for all layers combined.

Statistic	Site Area			
	Overall	SHU	MHU	DHU
RMS (mg/L)	0.06	0.04	0.06	0.08
Mean Residual (mg/L)	0.03	0.02	0.03	0.04

Overall, the model presents a conservative estimate of actual conditions present at the Site. For example:

- The model predicts the presence of chlorobenzene in the MHU while site data show no chlorobenzene in this area.
- Based on calibration results, the model uses a lower (slower) biodegradation rate than the Illinois Tiered Approach to Corrective Action Objectives (TACO) (35 IAC 742) standard.
- Maximum detected concentrations from 1980s to 2006 were used to calculate source concentrations over time for the slow source decay term. For some constituents, this resulted in higher 2006 concentrations than actual measured values.

6.2 Predicted Plume Extent in 2038

Chlorobenzene, 1,4-dichlorobenzene, 2,4-dichlorophenoxyacetic acid, and vinyl chloride plumes, while smaller in 2038, are predicted to still be present at the site. Tetrachloroethene, trichloroethene, and cis-1,2-dichloroethene plumes are predicted to get slightly larger by 2038 (Figures 34 to 38 for chlorobenzene, Figures 45 to 49 for 1,4-dichlorobenzene, Figures 56 to 60 for 2,4-dichlorophenoxyacetic acid, Figures 67 to 69 for PCE, Figures 76 to 78 for TCE, Figures 85 to 89 for 1,2-DCE, and Figures 96 to 100 for vinyl chloride).

6.3 Capture of 2038 Plumes by the GMCS

A qualitative evaluation of plume capture by the GMCS can be made by evaluating the following figures: Figures 34 to 38 for chlorobenzene, Figures 45 to 49 for 1,4-dichlorobenzene, Figures 56 to 60 for 2,4-dichlorophenoxyacetic acid, Figures 67 to 69 for PCE, Figures 76 to 78 for TCE, Figures 85 to 89 for 1,2-DCE, and Figures 96 to 100 for vinyl chloride. As can be seen, very little of the 2,4-D plume appears to discharge to the river (Figures 56 to 60), compared to the 2038 TCE plume (Figures 76 to 78).

Quantitatively, the percent of dissolved constituent mass flux (mass per time entering the river) captured by the GMCS was also determined for each constituent. For this purpose, the 2003 to 2038 segment of the model was run for each constituent with a) the GMCS in place and b) the GMCS off. The percent of mass flux captured by the GMCS in 2038 was then calculated (Figures 28 to 30, see next page).

Overall, when all modeled constituents are included, over 94% of the total plume mass flux that would have discharged to the river in 2038 without the GMCS is predicted to be captured by the GMCS.

When the highway dewatering system is shut down in 2010, flow from the aquifer to the river will increase, increasing the mass flux to the river. Eventually, however, the mass flux to the river will decrease as the effects of slow source decay overcome the effects of increased river discharge. By the time the system reaches steady state (about 2020), the mass flux to the river will be decreasing steadily and will continue to decrease as the source is depleted.

Almost all the total chlorinated ethene mass flux (combined PCE, TCE, DCE, and VC) is predicted to be captured by the GMCS in 2038 (94%). However, the mass flux and percent capture for each individual chlorinated solvent varied considerably as shown below.

Modeled Mass Flux To River in 2038 (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2- DCE	DCB	VC	TCE	PCE
<i>With GMCS OFF</i>	21,224	10,843	8,402	1,009	651	296	17	7
<i>With GMCS ON</i>	1,378	92	1,030	48	172	28	9	1

CB = chlorobenzene; DCB = 1,4-dichlorobenzene; 2,4-D = 2,4-Dichlorophenoxyacetic acid; PCE = tetrachloroethene; TCE = trichloroethene; 1,2-DCE = cis-1,2-dichloroethene; VC = vinyl chloride; kg/yr = kilograms per year.

Percent Mass Flux Captured by GMCS in 2038 (%)								
	All 7 COCs	2,4-D	CB	1,2- DCE	DCB	VC	TCE	PCE
<i>With GMCS ON</i>	94	99	88	95	74	91	48	79

CB = chlorobenzene; DCB = 1,4-dichlorobenzene; 2,4-D = 2,4-Dichlorophenoxyacetic acid; PCE = tetrachloroethene; TCE = trichloroethene; 1,2-DCE = cis-1,2-dichloroethene; VC = vinyl chloride; kg/yr = kilograms per year.

Although only 48% of the trichloroethene mass flux is predicted to be captured by the GMCS in 2038, this is a comparatively small plume compared to the mass flux of the other constituents (total mass flux of 17 kilograms per year of TCE going to the river or the GMCS compared to ~21,000 kilograms per year for all seven constituents).

Note that the GMCS captures the mass flux associated with other Site-R related COCs that were not included in this modeling study, such as, phenol, 3-nitrochlorobenzene, and 4 nitrochlorobenzene. The capture of these Site R compounds by the GMCS is not reflected in the percent capture table shown above.

6.4 Capture of Source Area Plumes by the GMCS

Quantitatively, the percent of dissolved constituent mass flux captured by the GMCS was also determined for each source area. For this purpose, all other source areas were removed and the 2003 to 2038 segment of the model was run with a) the GMCS in place and b) the GMCS off.

All Source Areas

Modeled mass flux to the river for all source areas was calculated as the sum of the mass fluxes to the river for individual SA1, SA2, WGK, and Clayton Chemical sources. Overall, when all modeled constituents are included, over 94% of the total plume mass flux that would have discharged to the river in 2038 without the GMCS is predicted to be captured by the GMCS.

Modeled Mass Flux To River with GMCS OFF (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	20,386	11,621	7,014	987	404	358	2	1
2010	19,825	11,030	7,001	958	438	387	8	2
2020	29,600	15,234	11,631	1,414	884	411	19	6
2030	25,187	12,891	9,948	1,201	772	348	20	8
2038	21,224	10,843	8,402	1,009	651	296	17	7

CB = chlorobenzene; DCB = 1,4-dichlorobenzene; 2,4-D = 2,4-Dichlorophenoxyacetic acid; PCE = tetrachloroethene; TCE = trichloroethene; 1,2-DCE = cis-1,2-Dichloroethene; VC = vinyl chloride; kg/yr = kilograms per year.

Modeled Mass Flux To River with GMCS ON (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	619	114	320	63	21	101	0.03	0.02
2010	688	83	481	23	55	46	0.7	0.1
2020	1,833	129	1,368	63	224	36	11	2
2030	1,608	109	1,199	56	199	32	10	2
2038	1,378	92	1,030	48	172	28	9	1

Percent Mass Flux Captured by GMCS (%)								
<i>With GMCS ON</i>	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	97	99	95	94	95	72	98	99
2010	97	99	93	98	88	88	92	95
2020	94	99	88	96	75	91	41	67
2030	94	99	88	95	74	91	49	79
2038	94	99	88	95	74	91	48	79

Sauget Area 1 Source Areas Only

For Sauget Area 1 sources only, overall, when all modeled constituents are included, 86% of the total plume mass flux that would have discharged to the river in 2038 without the GMCS is predicted to be captured by the GMCS.

Modeled Mass Flux To River with GMCS OFF (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	274	0	135	19	13	107	0.0001	0
2010	396	0.001	215	41	25	107	6	1
2020	1,124	0.01	805	77	92	132	16	3
2030	998	0.01	720	66	83	113	14	2
2038	854	0.01	618	56	72	95	12	2

CB = chlorobenzene; DCB = 1,4-dichlorobenzene; 2,4-D = 2,4-Dichlorophenoxyacetic acid; PCE = tetrachloroethene; TCE = trichloroethene; 1,2-DCE = cis-1,2-Dichloroethene; VC = vinyl chloride; kg/yr = kilograms per year.

Modeled Mass Flux To River with GMCS ON (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	142	0	43	14	4	81	0	0
2010	77	0.0001	29	8	2	37	0.6	0.1
2020	151	0.004	58	42	13	25	11	2
2030	141	0.004	57	38	13	22	10	2
2038	121	0.004	50	32	11	19	8	1

Percent Mass Flux Captured by GMCS (%)								
<i>With GMCS <u>ON</u></i>	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	48	97	68	26	73	25	98	98
2010	81	89	87	79	91	66	90	90
2020	87	39	93	45	86	81	29	31
2030	86	32	92	43	85	80	27	29
2038	86	32	92	43	85	80	27	29

Sauget Area 2 Source Areas Only – Combined

For Sauget Area 2 sources only, overall, when all modeled constituents are included, 98% of the total plume mass flux that would have discharged to the river in 2038 without the GMCS is predicted to be captured by the GMCS.

Modeled Mass Flux To River with GMCS OFF (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	18,458	11,621	6,491	0	346	0	0	0
2010	17,521	11,030	6,160	0	330	0	0	0
2020	24,523	15,234	8,835	0	455	0	0	0
2030	20,754	12,891	7,476	0	387	0	0	0
2038	17,452	10,843	6,289	0	321	0	0	0

CB = chlorobenzene; DCB = 1,4-dichlorobenzene; 2,4-D = 2,4-Dichlorophenoxyacetic acid; PCE = tetrachloroethene; TCE = trichloroethene; 1,2-DCE = cis-1,2-Dichloroethene; VC = vinyl chloride; kg/yr = kilograms per year.

Modeled Mass Flux To River with GMCS ON (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	321	114	200	0	8	0	0	0
2010	230	83	143	0	4	0	0	0
2020	377	129	242	0	6	0	0	0
2030	320	109	205	0	5	0	0	0
2038	269	92	173	0	4	0	0	0

Percent Mass Flux Captured by GMCS (%)								
<i>With GMCS <u>ON</u></i>	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	98	99	97	-	98	-	-	-
2010	99	99	98	-	99	-	-	-
2020	98	99	97	-	99	-	-	-
2030	98	99	97	-	99	-	-	-
2038	98	99	97	-	99	-	-	-

Sauget Area 2 Source Areas – Site R Only

For Sauget Area 2 Site R sources only, overall, when all modeled constituents are included, 99% of the total plume mass flux that would have discharged to the river in 2038 without the GMCS is predicted to be captured by the GMCS.

Modeled Mass Flux To River with GMCS OFF (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	18,337	11,621	6,370	0	346	0	0	0
2010	17,408	11,030	6,047	0	330	0	0	0
2020	24,265	15,234	8,576	0	455	0	0	0
2030	20,531	12,891	7,254	0	387	0	0	0
2038	17,265	10,843	6,102	0	321	0	0	0

CB = chlorobenzene; DCB = 1,4-dichlorobenzene; 2,4-D = 2,4-Dichlorophenoxyacetic acid; PCE = tetrachloroethene; TCE = trichloroethene; 1,2-DCE = cis-1,2-Dichloroethene; VC = vinyl chloride; kg/yr = kilograms per year.

Modeled Mass Flux To River with GMCS ON (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	295	114	174	0	8	0	0	0
2010	209	83	122	0	4	0	0	0
2020	330	129	194	0	6	0	0	0
2030	279	109	165	0	5	0	0	0
2038	235	92	139	0	4	0	0	0

Percent Mass Flux Captured by GMCS (%)								
<i>With GMCS <u>ON</u></i>	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	98	99	97	-	98	-	-	-
2010	99	99	98	-	99	-	-	-
2020	99	99	98	-	99	-	-	-
2030	99	99	98	-	99	-	-	-
2038	99	99	98	-	99	-	-	-

Sauget Area 2 Source Areas – Site O Only

For Sauget Area 2 Site O sources only, when all modeled constituents are included, 82% of the total plume mass flux that would have discharged to the river in 2038 without the GMCS is predicted to be captured by the GMCS.

Modeled Mass Flux To River with GMCS OFF (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	121	0	121	0	0	0	0	0
2010	113	0	113	0	0	0	0	0
2020	260	0	260	0	0	0	0	0
2030	222	0	222	0	0	0	0	0
2038	187	0	187	0	0	0	0	0

CB = chlorobenzene; DCB = 1,4-dichlorobenzene; 2,4-D = 2,4-Dichlorophenoxyacetic acid; PCE = tetrachloroethene; TCE = trichloroethene; 1,2-DCE = cis-1,2-Dichloroethene; VC = vinyl chloride; kg/yr = kilograms per year.

Modeled Mass Flux To River with GMCS ON (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	26	0	26	0	0	0	0	0
2010	21	0	21	0	0	0	0	0
2020	47	0	47	0	0	0	0	0
2030	41	0	41	0	0	0	0	0
2038	34	0	34	0	0	0	0	0

Percent Mass Flux Captured by GMCS (%)								
<i>With GMCS <u>ON</u></i>	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	79	-	79	-	-	-	-	-
2010	81	-	81	-	-	-	-	-
2020	82	-	82	-	-	-	-	-
2030	82	-	82	-	-	-	-	-
2038	82	-	82	-	-	-	-	-

Clayton Chemical Source Areas Only

For Clayton sources only, overall, when all modeled constituents are included, 98% of the total plume mass flux that would have discharged to the river in 2038 without the GMCS is predicted to be captured by the GMCS.

Modeled Mass Flux To River with GMCS OFF (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	1,562	0	308	967	32	251	2	1
2010	1,523	0	292	917	31	280	2	1
2020	2,216	0	537	1,337	57	279	3	3
2030	1,888	0	457	1,135	49	236	6	6
2038	1,589	0	385	953	40	201	5	5

CB = chlorobenzene; DCB = 1,4-dichlorobenzene; 2,4-D = 2,4-Dichlorophenoxyacetic acid; PCE = tetrachloroethene; TCE = trichloroethene; 1,2-DCE = cis-1,2-Dichloroethene; VC = vinyl chloride; kg/yr = kilograms per year.

Modeled Mass Flux To River with GMCS ON (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	87	0	16	49	1	21	0.03	0.02
2010	28	0	4	15	0.4	9	0.04	0.01
2020	50	0	16	21	1	11	0.09	0.03
2030	43	0	14	18	1	10	0.2	0.06
2038	37	0	12	16	1	9	0.2	0.05

Percent Mass Flux Captured by GMCS (%)								
<i>With GMCS ON</i>	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	94	-	95	95	96	92	98	99
2010	98	-	98	98	99	97	98	99
2020	98	-	97	98	98	96	97	99
2030	98	-	97	98	98	96	97	99
2038	98	-	97	98	98	96	97	99

W.G. Krummrich Source Areas Only

For WKG sources only, overall, when all modeled constituents are included, 28% of the total plume mass flux that would have discharged to the river in 2038 without the GMCS is predicted to be captured by the GMCS.

Modeled Mass Flux To River with GMCS OFF (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	92	0	80	0	12	0	0	0
2010	385	0	334	0	51	0	0	0
2020	1,735	0.0003	1,454	0	282	0	0	0
2030	1,548	0.0004	1,294	0	254	0	0	0
2038	1,329	0.0004	1,111	0	218	0	0	0

CB = chlorobenzene; DCB = 1,4-dichlorobenzene; 2,4-D = 2,4-Dichlorophenoxyacetic acid; PCE = tetrachloroethene; TCE = trichloroethene; 1,2-DCE = cis-1,2-Dichloroethene; VC = vinyl chloride; kg/yr = kilograms per year.

Modeled Mass Flux To River with GMCS ON (kg/yr)								
	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	69	0	61	0	9	0	0	0
2010	352	0	305	0	48	0	0	0
2020	1,256	0.0003	1,052	0	204	0	0	0
2030	1,103	0.0004	923	0	180	0	0	0
2038	951	0.0003	795	0	155	0	0	0

Percent Mass Flux Captured by GMCS (%)								
<i>With GMCS ON</i>	All 7 COCs	2,4-D	CB	1,2-DCE	DCB	VC	TCE	PCE
2006	25	55	24	-	27	-	-	-
2010	8	-	9	-	6	-	-	-
2020	28	19	28	-	28	-	-	-
2030	29	14	29	-	29	-	-	-
2038	28	14	28	-	29	-	-	-

Mass Flux Discussion

Results from the mass flux calculations suggest that in the year 2038, the GMCS will capture 94% of the total mass flux to the river that originates from the four modeled source areas (SA1, SA2, Krummrich, and Clayton). SA2 and Clayton show >98% capture rates for the years between 2010 and 2038. SA1 shows 86% capture rate in 2038.

The Krummrich source area shows a complex mass-flux-to-river relationship due to changing groundwater flow directions over time. In the early 2000s, the Krummrich plumes are oriented more north/south due to the influence of the Highway Dewatering System in East St. Louis (see Figures 32 and 33). Since this Highway Dewatering System's estimated flowrate was reduced significantly in the model in 2000, and then set to zero in 2010 (based on information that this system would be shut down in 2010), the Krummrich plume then takes a more westerly direction towards the river and results in an increase in mass flux over time, from a total of 352 kg/yr in 2010 to a maximum of 1256 kg/yr in 2020. The mass flux slowly declines over time due to the effects of source decay, and in the year 2038 the mass flux to the river is 951 kg/yr. Model results suggest that 28% of the Krummrich mass flux is captured by the GMCS in the year 2038.

The Krummrich scenario described above is heavily dependent on certain assumptions that cannot be verified at this time, such as the assumed highway dewatering flowrates over time and the degree of influence of the highway dewatering system on the Krummrich plumes.

Because of the way the transport model simulates source zones, a mathematical adjustment was required for three downgradient sources (CB for Site O in SA2 and CB and DCB for the Clayton source zone) because of the effects of upgradient plumes flowing into the source zones. This adjustment, described below, reduced, but did not eliminate the calculated mass flux from these source zones.

A detailed analysis of model output was performed to adjust these source terms to reflect upgradient sources, resulting in the following adjustment factors:

- Chlorobenzene source from Site O in SA2: Reduce source strength (and mass flux) by **35%**
- Chlorobenzene source from Clayton: Reduce source strength (and mass flux) by **39%**
- 1,4-Dichlorobenzene source from Clayton: Reduce source strength (and mass flux) by **37%**

The overall mass flux estimates did not change significantly. No other source zone/COC combinations appeared to be significantly affected by this issue, although a detailed analysis of the Site R source zone was not performed because the model assumes it is essentially all captured by the GMCS.

7.0 SENSITIVITY ANALYSIS

Sensitivity analyses are performed on calibrated groundwater models to identify the input parameters that have the most impact on the calibration and simulation results. In accordance with ASTM standard D 5611-94, sensitivity analysis was performed for chlorobenzene on the following parameters:

- Recharge (high and low);
- Hydraulic conductivity in all three Hydrogeologic Units and in the Shallow Hydrogeologic Unit (Layer 1 in the model) alone (high and low);
- River stage;
- Constant head cells (high and low);
- River bed conductance (high and low)
- Storativity (high and low);
- Rate constants (high and low);
- Dispersivity (high and low); and,
- Constant vs. decaying source concentration.

The range that was varied for each parameter was based on ranges in the underlying data for each parameter used in the sensitivity analysis.

The table below summarizes the discharge from the site to the river when various parameters were altered. Conclusions that can be drawn from this sensitivity analysis are:

- None of the parameters varied made a significant improvement to the model calibration and prediction; therefore, the original model parameters were retained.
- Although lowering the recharge rate to 5.8 in/yr improved the RMS and MR errors of the contaminant transport model, the flow model RMS and MR errors increased; RMS and MR errors of 1.1 ft and -0.7 ft, respectively were obtained for the flow portion of the model. Therefore, the recharge rate of 7.8 in/yr was retained in the model.
- Similarly, lowering the constant head cells resulted in RMS and MR errors of 0.7 ft and -0.2 ft, respectively for the flow model.
- Decreasing the hydraulic conductivities in all three layers also resulted in an increase in the RMS and MR errors of the flow model (1.5 ft and 0.9 ft, respectively).

SENSITIVITY RUN DESCRIPTION	OVERALL CHLOROBENZENE RMS ERROR (MG/L)	OVERALL CHLOROBENZENE MR ERROR (MG/L)	2006 MASS DISCHARGE TO RIVER (KG/YR)
BASELINE CASE	4.2	0.5	330
HIGHER Recharge: Recharge Increased from 7.8 inches/yr to 9.7 inches/yr	4.9	1.0	1,255

April 14, 2008

SENSITIVITY RUN DESCRIPTION	OVERALL CHLOROBENZENE RMS ERROR (MG/L)	OVERALL CHLOROBENZENE MR ERROR (MG/L)	2006 MASS DISCHARGE TO RIVER (KG/YR)
LOWER Recharge: Recharge Decreased from 7.8 inches/yr to 5.8 inches per yr	3.8	-0.1	127
HIGHER Hydraulic Conductivity In All Three Layers (K_x , K_y , and K_z increased 50 percent)	5.2	1.2	1,205
LOWER Hydraulic Conductivity In All Three Layers (K_x , K_y , and K_z reduced 50 percent)	3.9	-0.3	124
HIGHER Hydraulic Conductivity In Shallow Unit Only (K_x , K_y , and K_z increased by factor of 10)	6.7	1.0	411
LOWER Hydraulic Conductivity In Shallow Unit Only (K_x , K_y , and K_z reduced by factor of 10)	4.2	0.5	352
HIGHER River Stage: River Stage Increased from 391 ft MSL to 401 ft MSL (the high monthly average flow)	4.2	-0.7	21
LOWER River Stage: River Stage Decreased from 391 ft MSL to 383 ft MSL (the low monthly average flow)	5.8	1.6	2,303
HIGHER Constant Head: Constant Head Increased by 10 percent	6.9	2.0	525
LOWER Constant Head: Constant Head Decreased by 5 feet	3.9	0.3	227
HIGHER River Conductance: River Conductance multiplied by 2	4.2	0.5	355
LOWER River Conductance: River Conductance divided by 2	4.2	0.5	340
HIGHER Storativity: Specific Storage Increased from 0.0016 to 0.002 (high literature value)	4.2	0.5	329
LOWER Storativity: Specific Storage Decreased from 0.0016 to 0.0011 (low literature value)	4.2	0.5	331
HIGHER Rate Constant: Rate Constant Increased by factor of 2	4.0	-0.6	92
LOWER Rate Constant: Rate Constant Decreased by factor of 2	8.4	3.2	1,958

SENSITIVITY RUN DESCRIPTION	OVERALL CHLOROBENZENE RMS ERROR (MG/L)	OVERALL CHLOROBENZENE MR ERROR (MG/L)	2006 MASS DISCHARGE TO RIVER (KG/YR)
HIGHER Dispersivity: Dispersivity Increased by 50 percent (from 46.0 to 68.9)	4.2	0.5	335
LOWER Dispersivity: Dispersivity Decreased by 50 percent (from 46.0 to 23.0)	4.2	0.5	335
CONSTANT Source: Source concentrations corresponding to the 2000 stress period used as constant source concentrations	4.8	0.9	393

8.0 MODEL LIMITATIONS

The groundwater flow and contaminant transport models have the following key limitations:

- Variations in Shallow Hydrogeologic Unit are not incorporated into the flow model; the unit is assumed to have a constant hydraulic conductivity.
- The Mississippi River is simulated with idealized cross section and river bottom conductance values that do not account for local variability of river conductance.
- The contaminant transport model has difficulty matching observed concentrations in wells immediately adjacent to the GMCS and Site R.
- The pumping rates for the industrial and highway dewatering are constant rates, when in actuality, the rates likely varied substantially over the duration of the simulations.
- Only one parameter was changed at a time during the sensitivity analysis, and therefore the modeling analysis does not account for any combined effects of parameters that might have changed.
- Source decay for all constituents was treated as a generalized term based on data derived from chlorobenzene source zones.

9.0 REFERENCES

- American Society for Testing and Materials, 1998. "Standard Guide for Conducting a Sensitivity Analysis for a Ground-Water Flow Model Application", ASTM D 5611-94, Philadelphia, PA.
- American Society for Testing and Materials, 2000. "Standard Guide for Subsurface Flow and Transport Modeling", ASTM D 5880-95, Philadelphia, PA.
- Baker, W.H. Jr., 1972. *Ground-Water Levels and Pumpage in the East St. Louis Area, Illinois, 1967-1971*, Illinois State Water Survey, Urbana, Illinois.
- Clement, T.P., 1997. *RT3D - A Modular Computer Code for Simulating Reactive Multi-Species Transport in 3-Dimensional Groundwater Aquifers*. Pacific Northwest National Laboratory, Richland, WA, USA. PNNL-11720
- Collins, M.A. and S.S. Richards, 1986. *Ground-Water Levels and Pumpage in the East St. Louis Area, Illinois, 1978-1980*, Illinois State Water Survey, Urbana, Illinois.
- Ecology and Environment, Inc., 1988. "Expanded Site Investigation Dead Creek Project Sites at Cahokia/Sauget, Illinois", Prepared for Illinois Environmental Protection Agency by Ecology and Environment, Inc., Chicago, Illinois, May 1988.
- Emmons, J.T., 1979. *Ground-Water Levels and Pumpage in the East St. Louis Area, Illinois, 1972-1977*, Illinois State Water Survey, Urbana, Illinois.
- Groundwater Services, Inc., 2001. "Source Evaluation Study", Prepared for Solutia Inc. by Groundwater Services, Inc., Houston, Texas, May 21, 2001.
- Groundwater Services, Inc., 2002. "Preliminary results of volatile organic compound and semi volatile organic compound groundwater transport analysis and comparison to ecological benchmark, W.G. Krummrich Plant, Sauget, Illinois" in "Focused Feasibility Study Interim Groundwater Remedy Sauget Area 2 Sites O, Q, R and S", Prepared for Solutia Inc. by Groundwater Services, Inc., Houston, Texas, November 25, 2002.
- Groundwater Services, Inc., 2003. "Sauget Area 2 Focused Feasibility Study", Prepared for URS Corp. by Groundwater Services, Inc., Houston, Texas, November 20, 2003.
- Groundwater Services, Inc., 2004. "Time to Clean Estimates", in "RCRA Corrective Measures Study (CMS) Solutia Inc. W. G. Krummrich Facility Sauget, Illinois". Prepared for Solutia Inc. by Groundwater Services, Inc., Houston, Texas, August 27, 2004.
- Groundwater Services, Inc., 2005. "Results of DNAPL Characterization and Remediation Study", Prepared for Solutia Inc. by Groundwater Services, Inc., Houston, Texas, January 21, 2005.
- Groundwater Services, Inc., 2006a. "Groundwater Modeling Plan", Prepared for URS Corporation by Groundwater Services, Inc., Houston, Texas, March 27, 2006.
- Groundwater Services, Inc., 2006b. "Regional Groundwater Flow Model American Bottoms Aquifer", Prepared for URS Corporation by Groundwater Services, Inc., Houston, Texas, October 27, 2006.
- McDonald, M.G. and A. Harbaugh, 1988. *A Modular Three Dimensional Finite-Difference Groundwater Flow Model*, Techniques of Water Resources Investigations 06-A7, USGS.
- Menzie-Cura and Associates, Inc., 2000. "Ecological Risk Assessment for Sauget Area 1 Sauget St. Clair County, Illinois", Prepared for Solutia Inc. by Menzie-Cura and Associates, Inc., Chelmsford, Massachusetts, December 8, 2000.
- Midwest Rubber, 1969. "General Plot Plan of East St. Louis Plant", Midwest Rubber Reclaiming Co. September 24, 1969. Figure.
- Monsanto, date unknown_a. "Site Development River Property Plot Long Range Plan", Monsanto Chemical Company. Figure.
- Monsanto, date unknown_b. "General Plant Map", Monsanto Chemical Company. Figure.

- Newell, C.J., J. Gonzales, and R. McLeod, 1996. *BIOSCREEN Natural Attenuation Decision Support System, Version 1.3*, U.S. Environmental Protection Agency, EPA/600/R-96/087, www.epa.gov/ada/kerrlab.html.
- Olson, R.D. and E.W. Sanderson, 2000. *Dewatering Well Assessment at Five Sites in the East St. Louis Area*, Illinois, Illinois State Water Survey, July 2000.
- Personal communication with Steven D. Smith of Solutia Inc., 2007.
- Reitz, G.E. Jr., 1968. *Ground-Water Levels and Pumpage in the East St. Louis Area, Illinois, 1962-1966*, Illinois State Water Survey, Urbana, Illinois.
- Ritchey, J.D. and R.J. Schicht, 1982. "Ground-Water Management in the American Bottoms, Illinois," State, County, Regional, and Municipal Jurisdiction of Ground-Water Protection, Proceedings of the Sixth National Ground-Water Quality Symposium, Atlanta, Georgia, September 14-22, 1982, National Water Well Association.
- Ritchey, J.D., R.J. Schicht, and L.S. Weiss, 1984a. *Part C. Existing and Future Ground Water Levels*, Illinois State Water Survey, Urbana, Illinois.
- Ritchey, J.D., R.J. Schicht, and L.S. Weiss, 1984b. *Part D. Evaluation of Alternative Measures*, Illinois State Water Survey, Urbana, Illinois.
- Ritchey, J.D., R.J. Schicht, and L.S. Weiss, 1984c. *Part E. Digital Flow Model Description and User's Guide*, Illinois State Water Survey, Urbana, Illinois.
- Roux Associates, Inc., 2001. "Engineering Evaluation/Cost Analysis Remedial Investigation/Feasibility Study Sauget Area 1 Sauget and Cahokia, Illinois", Prepared for Solutia Inc. by Roux Associates, Inc., Houston, Texas, June 9, 2001.
- Schicht, R.J. and A.G. Buck, 1995. *Ground-Water Levels and Pumpage in the Metro-East Area, Illinois, 1986-1990*, Illinois State Water Survey, Urbana, Illinois.
- Schicht, R.J. and E.G. Jones, 1962. *Ground-Water Levels and Pumpage in East St. Louis Area, Illinois, 1890-1961*, Illinois State Water Survey, Urbana, Illinois.
- Schicht, R.J., J.D. Ritchey, and L.S. Weiss, 1984a. *Part A. Ground-Water Levels and Pumpage*, Illinois State Water Survey, Urbana, Illinois.
- Schicht, R.J., J.D. Ritchey, and L.S. Weiss, 1984b. *Part B. The American Bottoms Digital Ground Water Flow Model*, Illinois State Water Survey, Urbana, Illinois.
- Solutia, 1999, "1998 Evaluation of Ground-Water Quality Conditions at the W.G. Krummrich Plant," Solutia Inc., September 30, 1999.
- Solutia, 2002, "Focused Feasibility Study Interim Groundwater Remedy Sauget Area 2 Sites O, Q, R, and S," Solutia Inc., March 31, 2002.
- TRRP, 2007. Texas Risk Reduction Program, <http://www.tceq.state.tx.us>.
- Waterloo Hydrogeologic, 2006. *Visual MODFLOW User's Manual*, Waterloo Hydrogeologic, Waterloo, Ontario.
- URS Corporation, 2002. "CA 750 Migration of Contaminated Groundwater Under Control W. G. Krummrich Plant", Maryland Heights, Missouri, December 2002.
- URS Corporation, 2004. "Remedial Investigation/Feasibility Study Report Sauget Area 2 Sauget, Illinois", URS Corporation, St. Louis, January 30, 2004.
- URS Corporation, Groundwater Services, Inc., and TRC, 2004. "RCRA Corrective Measures Study (CMS) Solutia Inc. W. G. Krummrich Facility Sauget, Illinois", URS Corporation, St. Louis, Missouri, Groundwater Services, Inc., Houston, Texas, and TRC, August 27, 2004.
- URS Corporation, 2006. "Sauget Area 2 Supplemental investigation Phase 2/3", URS Corporation, St. Louis, Missouri, 2006.
- URS Corporation, 2007. Access database.
- Xu, M. and Y. Eckstein, 1995, "Use of Weighted Least-Squares Method in Evaluation of the Relationship Between Dispersivity and Scale", *Ground Water*, 33(6): 905-908.